Oscillatory Galvanomagnetic Properties of Antimony Single Crystals at Liquid Helium Temperatures

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Measurements of the Hall coefficient and transverse magnetoresistance have been made on antimony single crystals at liquid helium temperatures and in magnetic fields up to 25 kilogauss. Both these properties exhibit oscillations which are periodic in reciprocal magnetic field. For a given orientation of the crystal axes relative to the magnetic field, the period of oscillation is the same for both these galvanomagnetic effects. The observed periods are in good agreement with the values found in the de Haas-van Alphen effect of antimony. The magnetic field dependence of the Hall coefficient was also examined at 78°K and 300°K. It was found that at 78°K the Hall coefficient already exhibits marked field dependence. Small amounts of impurities were found to have a marked effect on both the magnitude and field dependence of the Hall coefficient at low temperatures.

INTRODUCTION

EXPERIMENTS have shown that the galvanomagnetic and thermomagnetic properties of some of the metals which exhibit the de Haas-van Alphen effect also show oscillatory behavior as a function of magnetic field, H. Prior to the present work the correlation for the period of oscillation in H^{-1} had been established for bismuth,[1–5] graphite,[6,7] and zinc.[6,8] These metals are characterized by relatively long periods of oscillation in so far as the de Haas-van Alphen effect is concerned. On the other hand, antimony, which also exhibits the de Haas-van Alphen effect, has a relatively short period of oscillation[9] (of the order of fifty times smaller than that for Bi, Zn, or graphite). In general the amplitude of the susceptibility oscillations decreases as the period of oscillations decreases, so that it was of interest to see if the corresponding oscillatory galvanomagnetic effects could be observed in antimony. This paper concerns itself primarily with the measurements of the magnetic field dependence of the Hall coefficient and the transverse magnetoresistance of Sb single crystals in fields up to 25 kilogauss at liquid helium temperatures. A preliminary report[10] of the discovery of the magnetoresistance and Hall effect oscillations has already been given.

EXPERIMENTAL DETAILS

A. Crystals

The antimony single crystals used for most of these experiments (Sb I–Sb IV) were cleaved from a crystal kindly donated and grown by W. Zimmerman, III of the Crystal Branch, U. S. Naval Research Laboratory. The original material, as obtained from the Bradley Mining Company, San Francisco, California, had a purity of 99.997 percent. Zone refinement made the purity of the final crystal better than 99.999 percent. Cleaving the crystal under liquid nitrogen readily located the trigonal axis. Then the series of plates of about 0.5 mm thickness were cleaved from the large crystal. For each of these plates, the trigonal axis was perpendicular to the face of the plate. Examination of these crystals showed that some twinning had resulted since three sets of lines making angles of 60° with each other were barely visible. These lines allowed the binary axis to be located relative to the long dimension of the experimental rectangular specimens cut from the plates by an air stream containing powdered abrasive. The length of each rectangle was 10 mm, while the width was 2 mm. Thickness of individual specimens will be given when the results are presented. The long dimension was mounted vertically in all the experiments.

One of the specimens (Sb V) used for these experiments was prepared in the above manner from a crystal kindly donated by Dr. E. I. Salkovitz, Metal Physics Branch, Naval Research Laboratory. The original material for this crystal was Johnson-Matthey antimony (Lab. No. 4470) which had a purity of 99.92 percent (by difference).

B. Magnet

Horizontal magnetic field strengths up to 25 kilogauss were supplied by an A. D. Little electromagnet capable of rotation about a vertical axis. The five and three-quarter inch diameter pole pieces were separated by a gap of one and three-quarter inches. A nuclear fluxmeter was used to calibrate the magnet to an accuracy of 0.02 percent.

C. Measurement Technique

Current and potential leads were attached to each specimen with low melting-point solder. The measuring current was always parallel to the long dimension of

[1] P. B. Alers and R. T. Webber, Phys. Rev. **91**, 1060 (1953).
[2] T. G. Berlincourt, Phys. Rev. **91**, 1277 (1953).
[3] Reynolds, Leinhardt, and Hemstreet, Phys. Rev. **93**, 247 (1954). See also L. C. Brodie, Phys. Rev. **93**, 935 (1954).
[4] M. C. Steele and J. Babiskin, Phys. Rev. **94**, 1394 (1954).
[5] J. Babiskin and M. C. Steele, Phys. Rev. **96**, 822 (1954).
[6] T. G. Berlincourt and J. K. Logan, Phys. Rev. **93**, 348 (1954).
[7] T. G. Berlincourt and M. C. Steele (to be published).
[8] N. M. Nachimovich, J. Phys. U.S.S.R. **6**, 111 (1942).
[9] D. Shoenberg, Proc. Roy. Soc. (London) **245**, 1 (1952).
[10] M. C. Steele, Phys. Rev. **98**, 1180(A) (1955).

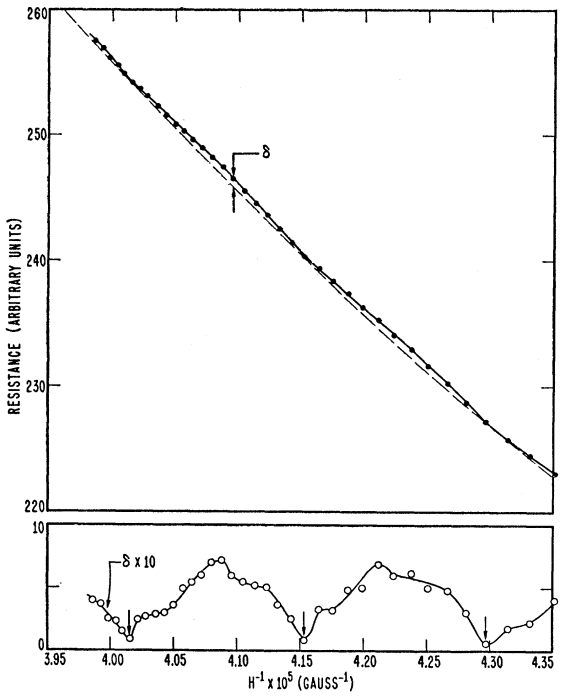

FIG. 1. Magnetoresistance of Sb I as a function of H^{-1} at 1.52°K. H was perpendicular to the trigonal axis and made an angle of 25° with a binary axis.

the specimens. The two potential probes used to measure resistance were on the same edge of the crystal, separated by a distance of about 3 mm. A third potential probe was located on the opposite edge to measure Hall voltages. Except for one experiment, Hall effect measurements were made only with H parallel to the trigonal axis. This geometry was ascertained by the visual location of the trigonal axis after the crystal was mounted. Attempts to locate the trigonal axis from magnetoresistance measurements proved to be an interesting problem in itself since the results depended very strongly upon the angle between a binary axis and the electric current. This had already been observed by Rausch[11] in his work on Sb single crystals down to liquid nitrogen temperatures. Our results support his conclusions and extend the rotation measurements to 4.21°K.

The Hall coefficient, A, is defined by the equation:

$$A=10^8Vt/IH, \tag{1}$$

where A is in cm³/coulomb; H is in gauss; the measuring current, I, is in amperes; the Hall potential, V, is in volts, and the crystal thickness, t, is in centimeters. Throughout these experiments the measuring current was either 200 or 400 milliamperes. Typical Hall voltages ranged from about 50 to 15 microvolts as the magnetic field was decreased from 25 to 6 kilogauss. These voltages were measured to an accuracy of 0.05 microvolt with a six-dial potentiometer in conjunction with a photoelectric galvanometer. Magnetoresistive components of the transverse voltages were separated from the Hall components by taking two sets of measurements in which the direction of H is changed by 180°. If we denote by $V(H)$ and $V(-H)$ the voltages measured in this way, then it is assumed that

$$2V_\rho=V(H)+V(-H), \tag{2}$$

$$2V_A=V(H)-V(-H), \tag{3}$$

where V_ρ is the magnetoresistance voltage component and V_A is the Hall voltage. This resolution supposes that the magnetoresistance is an even function of H. Measurements from the resistance probes confirmed this supposition over the range of field and temperature used. From Eqs. (2) and (3), simultaneous values of Hall coefficient and magnetoresistance are obtained. This is useful for comparing the relative values of the period and phase of the oscillations in these properties.

EXPERIMENTAL RESULTS

(A) Sb I

The first experiments with these crystals were restricted to a measurement of the magnetoresistance (from the resistance probes) as a function of H. Figure 1 shows the results at $T=1.52$°K for Sb I plotted as a function of H^{-1}. This crystal had $t=0.58$ mm. The angle, ψ, between the specimen length and a binary axis was 5°. H was perpendicular to the trigonal axis and made an angle of 25° with a binary axis. In order to emphasize the oscillatory nature of the resistance, the difference δ between the smooth dashed envelope curve and the solid curve connecting the experimental points is also plotted in Fig. 1. Our subsequent analysis will show that the δ curve is periodic in H^{-1}. Over the range of field shown in Fig. 1 the maximum value of the amplitude of the oscillating component ($\delta/2$) is only 0.15 percent of the total resistance. It is evident from the structure in the δ curve of Fig. 1 that there may be more than one oscillating term contributing to the phenomenon at this particular orientation.

(B) Sb IV

For this specimen t was 0.44 mm and ψ was 15°. The Hall coefficient, A, at $T=1.57$°K is plotted as a function of H^{-1} in Fig. 2. H was parallel to the trigonal axis (to within 3°). The oscillations in A are very distinct; however, the modulation in the amplitude of the oscillations suggests that there is more than one oscillating term present. At 25 kilogauss, the amplitude of the oscillatory component of A is 0.6 percent of the mean value of A. Figure 3 shows the magnetoresistance as a function of H^{-1} under the same conditions as for Fig. 2. In fact, the data in Fig. 3 are obtained from the Hall effect measurements through Eq. (2). Again the oscillating component is easily discernible from the

[11] K. Rausch, Ann. Physik **1**, 190 (1947).

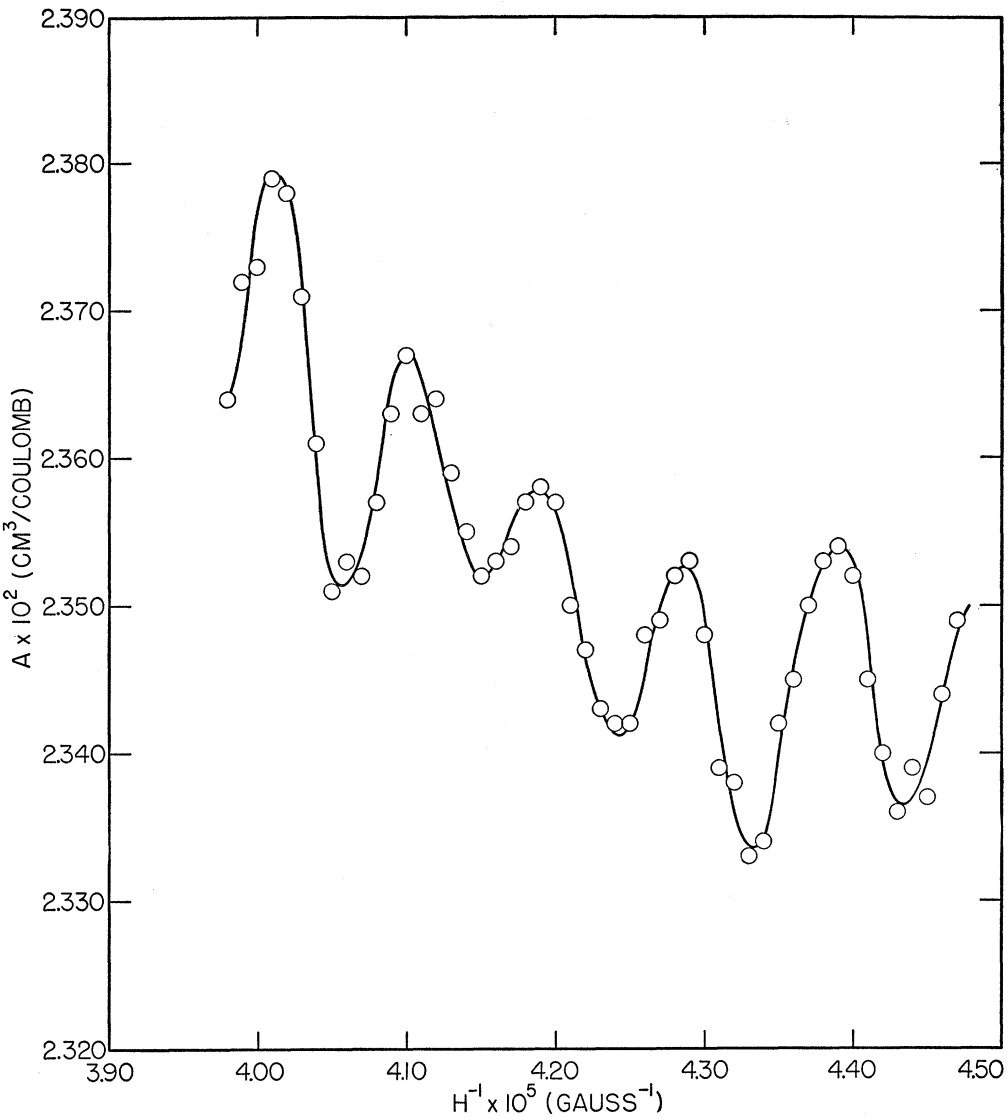

FIG. 2. Field dependence of the Hall coefficient of Sb IV at 1.57°K. H was parallel to the trigonal axis.

total resistance. The dashed lines are the envelope curves drawn through the extremities of the data. At 25 kilogauss the amplitude of the oscillatory components of resistance is 0.3 percent of the total resistance.

Hall coefficient data for Sb IV were also taken at 78°K and 300°K. These results (together with those at 4.21°K) showing A as a function of H are given in Fig. 4. All the data in Fig. 4 were taken with H parallel to the trigonal axis. For this orientation, A is positive (abnormal) over the entire range of temperature and magnetic field strength investigated. The high-field portion of the 4.21°K curve is dashed to indicate that A underwent oscillations in that region. Whereas the 300°K data indicated practically no field dependence, the 78°K data show a definite change in A as a function of H. The sign and magnitude of A at 300°K is in good agreement with the work of Leverton and Dekker.[12]

Data on the variation of resistance as a function of the angle between the trigonal axis and H were taken at 300°K, 78°K, and 4.21°K. The results for Sb IV at $H=25$ kilogauss are shown in Fig. 5 where $\Delta\rho=\rho_H-\rho_0$ and ρ_0 is the resistance in zero field at the particular temperature. Aside from the fact that the minimum in resistance did not occur when H was parallel to the trigonal axis, it can be seen that at 4.21°K, there is a marked departure from the simpler angular dependence exhibited at the higher temperatures. However, it is noted that even in going from 300°K to 78°K, the position of the maximum in resistance shifted by 15° of angle. On the other hand, the position of the minimum

[12] W. F. Leverton and A. J. Dekker, Phys. Rev. **80**, 732 (1950).

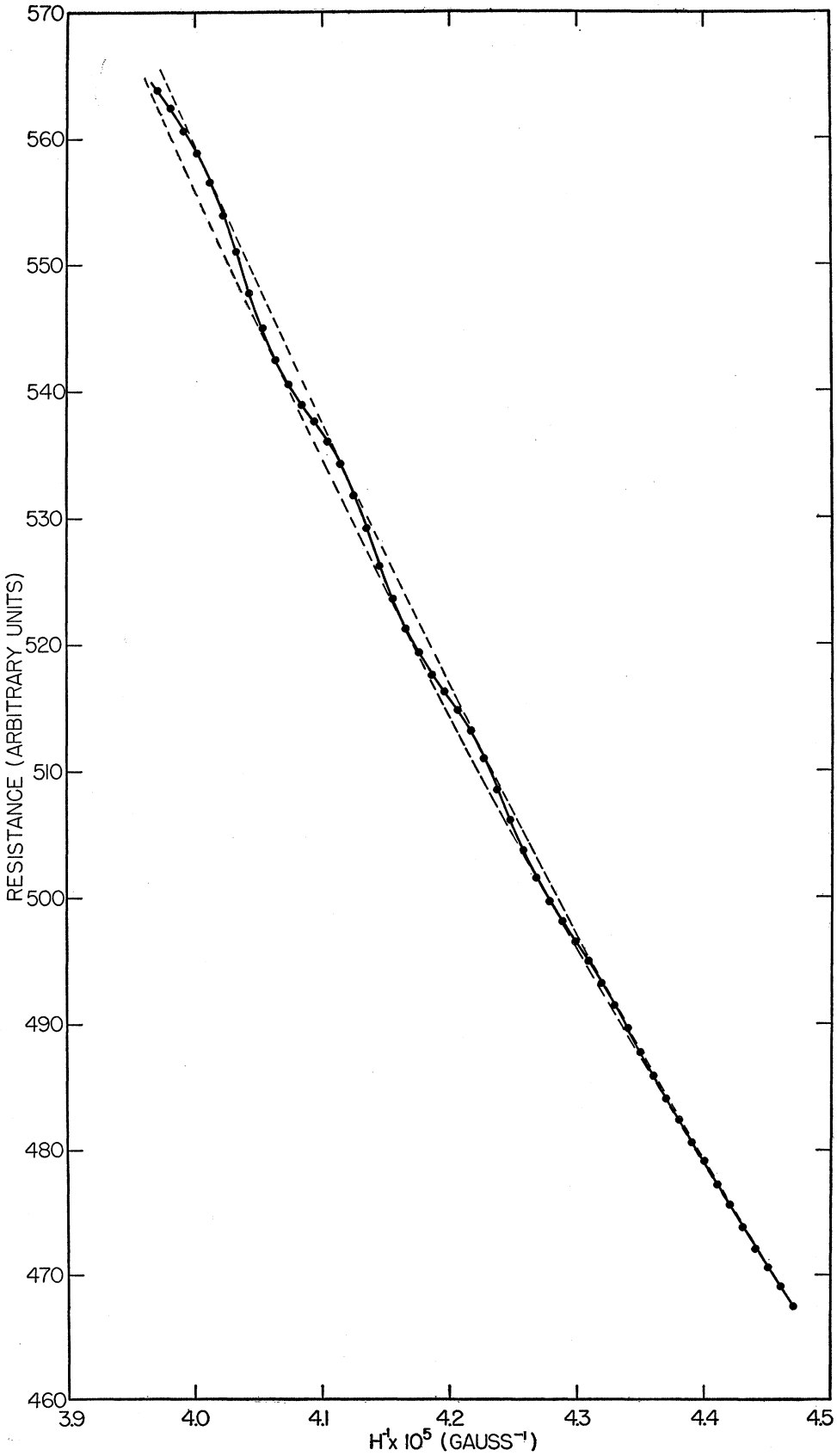

FIG. 3. Magnetoresistance of Sb IV at 1.57°K. H was parallel to the trigonal axis.

remained unchanged over the entire temperature range. Distortion of the rotation diagram from a sine curve is already evident at 78°K. This is in qualitative agreement with Rausch's[11] results on an antimony crystal having $\psi=2.8°$ (whereas our Sb IV had $\psi=15°$).

Hall effect and magnetoresistance data were also taken at the magnet setting corresponding to the minimum in resistance. For these data there was a 15° angle between H and the trigonal axis. The Hall coefficient as a function of H^{-1} at 4.214°K and 1.549°K is shown in Fig. 6 for this orientation. Although the oscillatory character is evident, the curves are far more complicated than that shown in Fig. 2. Corresponding magnetoresistance data [obtained from the Hall effect probes through Eq. (2)] are shown in Fig. 7. In addition, the oscillatory component of the magnetoresistance has been separated and plotted at the bottom of Fig. 7. These data give a vivid picture of the temperature dependence of the oscillating component of the magnetoresistance. Surprisingly enough, for this orientation, the magnetoresistance oscillations do not exhibit the complicated structure shown by the Hall coefficient.

(C) Sb V

This was the specimen prepared from Johnson-Matthey antimony. The major impurities were Pb (0.0275 percent) and As (0.025 percent). Data were taken on this crystal for two reasons. Firstly, it was thought advisable to be able to get the oscillatory effects on specimens from two entirely different sources. Secondly, it was an opportunity to study how small amounts of impurities would affect the galvanometric properties, particularly the oscillatory behavior, at low temperatures.

This specimen had $t=0.685$ mm and $\psi=90°$. The trigonal axis was perpendicular to the face of the plate, just as for the other specimens. Rotation diagrams for the magnetoresistance (at $H=25$ kilogauss) are shown in Fig. 8. It is interesting to note that at all three temperatures the minimum in resistance corresponded to H being parallel to the trigonal axis. Thus, for this particular type of crystal geometry, the position of the trigonal axis could be located from magnetoresistance measurements. Rausch's[11] results at 78°K on an antimony crystal with $\psi=87.8°$ are in good agreement with the present data (even though his data were taken with $H=10.1$ kilogauss).

Hall-effect data were taken with H parallel to the trigonal axis. Figure 9 gives the results at $T=1.549$°K. Although the oscillatory nature of A is evident from this curve, there are several irregularities as compared to the results for Sb IV (shown in Fig. 2). Most striking is the steepness of the envelope curve (dashed) over the range of field shown (22–25 kilogauss). The mean value of A changed by 12 percent while for Sb IV there

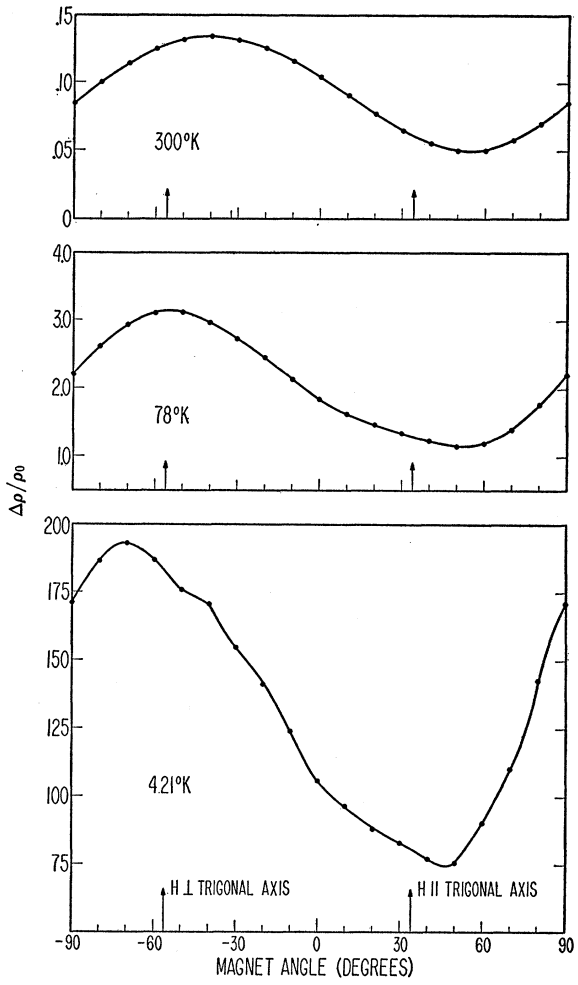

FIG. 5. Resistance of Sb IV as a function of magnet angle ($H=25$ kilogauss).

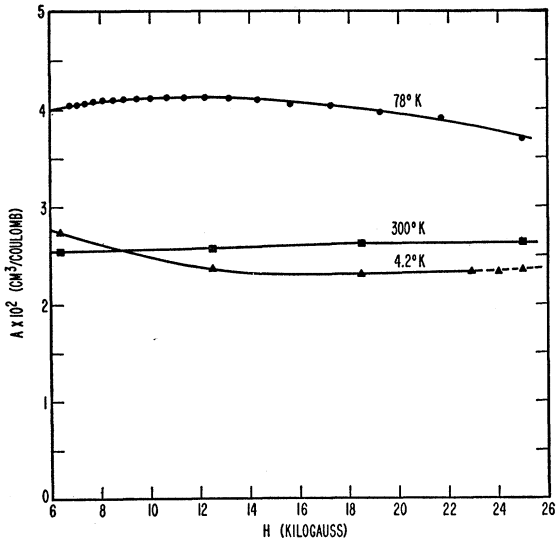

FIG. 4. Field dependence of the Hall coefficient of Sb IV. H was parallel to the trigonal axis.

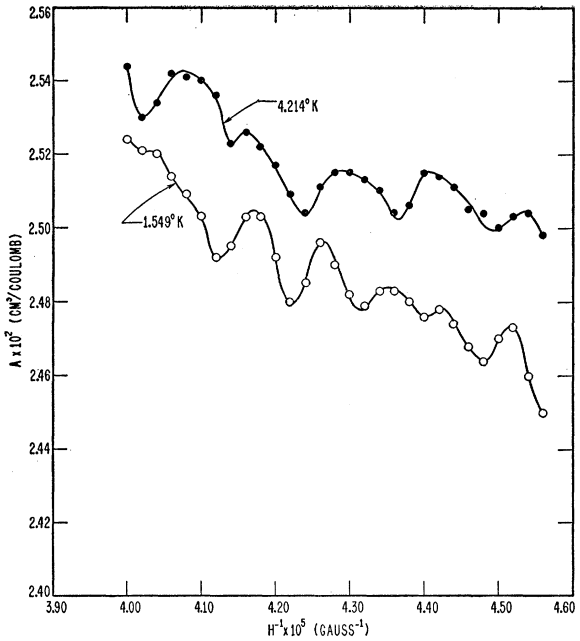

FIG. 6. Hall coefficient of Sb IV when H was at an angle of 15° to the trigonal axis.

was only a 1.5 percent change. Further, the magnitude of A at 25 kilogauss is 60 percent larger than that for Sb IV. Both of these characteristics are most likely due to impurities, but further work is needed to establish this conjecture. Finally, for this crystal the amplitude of the oscillatory component of A is only 0.2 percent of the mean value of A as compared to 0.6 percent for Sb IV.

Since the magnetic field dependence of A was so much stronger for Sb V in high fields, it was thought profitable to make a more detailed study of this behavior over a wider range of field and temperature. The results of such experiments (for Sb V) are given in Fig. 10 where A is plotted as a function of H at three temperatures. H was parallel to the trigonal axis for these data. At 300°K, A is field-independent; at 78°K there appears a field dependence qualitatively similar to that shown in Fig. 4, but the magnitude of A is different for the two cases; at 4.2°K the difference between the two curves is more evident.

DISCUSSION

(A) Period of Oscillations

Sb I magnetoresistance.—From Fig. 1 the principle period of oscillation of the δ curve is 14.1×10^{-7} gauss^{-1}. We shall designate the period of oscillation in H^{-1} as β/E_0 because this is the usual nomenclature in de Haas-van Alphen work. There β is the double effective Bohr magneton (involving effective masses for the electrons) and E_0 is the chemical potential (Fermi energy) of the pertinent de Haas-van Alphen electrons (or holes) measured from the bottom of the significant zone for electrons (or from the top of the zone for holes). From the ellipsoid scheme proposed by Shoenberg[9] for antimony, we find that for our orientation (H perpendicular to the trigonal axis and at an angle of 25° to a binary axis) there would be three values of β/E_0. They are

$$\beta_1/E_0=14.5\times10^{-7}\ \text{gauss}^{-1},$$
$$\beta_2/E_0=\ 7.7\times10^{-7}\ \text{gauss}^{-1},$$
$$\beta_3/E_0=\ 5.9\times10^{-7}\ \text{gauss}^{-1}.$$

The value for β_1/E_0 is in good agreement with our value of 14.1×10^{-7} gauss^{-1}. Our results also indicate that there are subordinate oscillatory terms present, but the data do not warrant making a quantitative comparison to the two other periods of oscillation. Such a detailed study would require another investigation.

Sb IV Hall coefficient and magnetoresistance.—From Fig. 2, β/E_0 for the Hall coefficient oscillations is $9.8\pm0.2\times10^{-7}$ gauss^{-1}. From Fig. 3 β/E_0 for the magnetoresistance oscillations is also $9.8\pm0.2\times10^{-7}$ gauss^{-1}. Thus, within experimental error both these oscillations have the same period. For H parallel to the trigonal axis (the orientation for these measurements) Shoenberg's[9] three oscillatory terms, all have the same period, $\beta/E_0=10.0\times10^{-7}$ gauss^{-1}. Again this is in good agreement with our results. The curve in Fig. 2 suggests

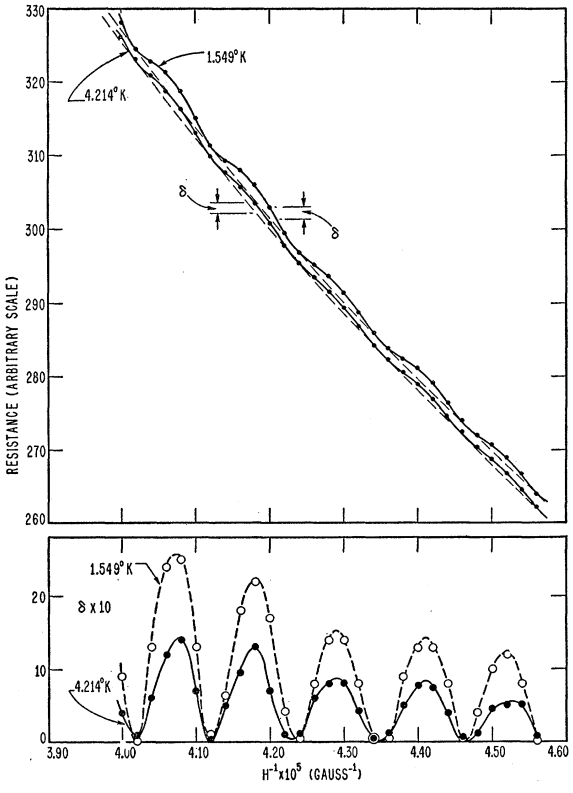

FIG. 7. Magnetoresistance of Sb IV when H was at an angle of 15° to the trigonal axis.

that there may be another oscillatory term present, but this might be due to uncertainties of several degrees in orienting the crystal with respect to H. Peculiarly enough, the magnetoresistance data in Fig. 3 do not show such a modulation of the oscillation amplitude.

(B) Relative Phase of Oscillations

From Figs. 2 and 3, we find that Hall coefficient oscillation maxima occur before the resistance maxima by about 2×10^{-7} gauss^{-1}. There is a good deal of uncertainty about this phase difference because of the arbitrary way in which the envelope curves are drawn and the aspect of beats in Fig. 2. However, the data are given so as to allow some comparison with the results on other materials. In terms of H^{-1}, the magnetoresistance maxima lag the Hall coefficient maxima by roughly 0.4π. Berlincourt and Steele[7] had found that for graphite, magnetoresistance minima lag Hall coefficient minima by about $\pi/4$. Unpublished data of Overton and Berlincourt on bismuth have shown zero phase difference between magnetoresistance and Hall coefficient minima. In light of the different results for three materials no empirical generalization can be made. A detailed model that takes into account the contributions of both holes and electrons is needed to describe each metal individually.

Since the mean value of the Hall coefficient is itself field dependent, it is of interest to see how this is related to the magnetoresistance. A significant function to

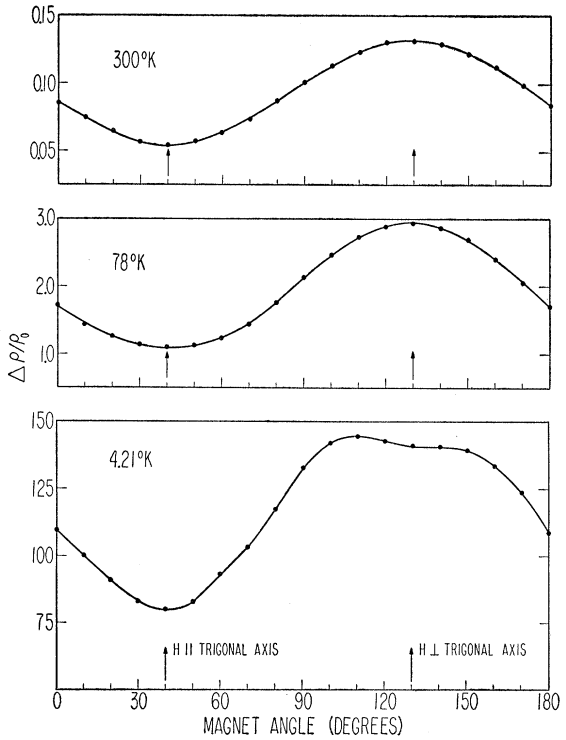

FIG. 8. Resistance of Sb V as a function of magnet angle ($H=25$ kilogauss).

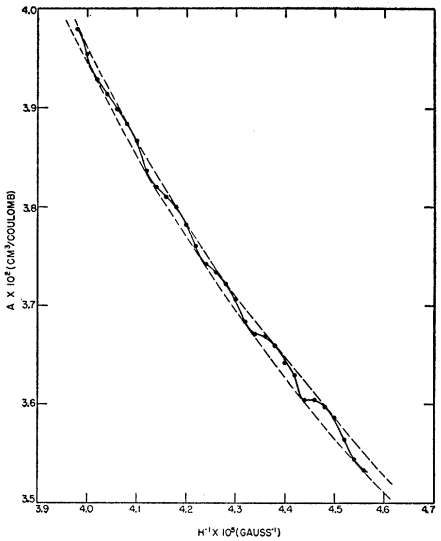

FIG. 9. Field dependence of the Hall coefficient of Sb V at 1.549°K. H was parallel to the trigonal axis.

examine is the product $A\sigma$, where σ is the electrical conductivity. For the simple two-band model, this product is a function of the mobilities and numbers of holes and electrons. The magnetic field dependence of $A\sigma$ might therefore supply more fundamental information than would analyses of the individual variations with H. The voltages, V_A and V_ρ, given in Eqs. (2) and (3), are proportional to AH and $1/\sigma$ respectively, so that

$$V_A/V_\rho \propto A\sigma H. \tag{4}$$

Figure 11 shows V_A/V_ρ plotted as a function of H^{-1} for Sb IV. The data for this graph were taken from the same experiment that gave Figs. 2 and 3. Hence, H was parallel to the trigonal axis and T was 1.57°K. The oscillations in $A\sigma H$ as a function of H^{-1} are clearly separable from the total value. These oscillations are periodic in H^{-1} and have $\beta/E_0=9.5\pm0.2\times10^{-7}$ gauss^{-1}. Another interesting feature of this graph is that the mean value of $A\sigma H$ is quite accurately a linear function of H^{-1} over the range shown in Fig. 11. On the basis of Borovik's[13] analysis of Hall effect and magnetoresistance effect data, one could infer from this linearity that the number of holes are equal to the number of electrons. To show this we follow Borovik and write

$$A\sigma H=\left(\frac{n_1\phi_1^2}{1+\phi_1^2}-\frac{n_2\phi_2^2}{1+\phi_2^2}\right)\Big/\left(\frac{n_1\phi_1}{1+\phi_1^2}+\frac{n_2\phi_2}{1+\phi_2^2}\right), \tag{5}$$

$$\phi_1=eH\tau_1/m_1c;\quad \phi_2=eH\tau_2/m_2c,$$

where $-e$ is the electronic charge; n_1 is the number of holes; n_2 is the number of electrons; m_1 and m_2 are the

[13] E. S. Borovik, J. Exptl. Theoret. Phys. (U.S.S.R.) **23**, 83 (1953).

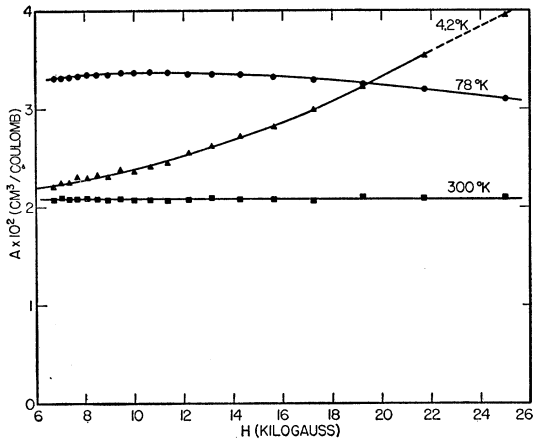

FIG. 10. Field dependence of the Hall coefficient of Sb V for H parallel to the trigonal axis.

effective masses of the holes and electrons respectively, and τ_1 and τ_2 are the respective mean collision times with the lattice. Equation (5) is based on the two-band model of an isotropic metal, whereas antimony is certainly anisotropic. However, it does provide a basis for a qualitative comparison between theory and experiment. The anisotropy would introduce the mass tensor, but the principle functional relations should retain their form. For $\phi_1, \phi_2 \gg 1$ (strong fields) and $n_1 \neq n_2$, Eq. (5) becomes

$$A\sigma H \sim (n_1 - n_2) eH \Big/ c\left(\frac{n_1 m_1}{\tau_1} + \frac{n_2 m_2}{\tau_2}\right). \quad (6)$$

This says that $A\sigma H$ would be increasing linearly with H for strong fields. Our data for Sb (in strong fields) do not show such behavior so we will examine the case $n_1 = n_2$. Then, at any field value, Eq. (5) becomes

$$A\sigma H = (\phi_1 - \phi_2)/(1 + \phi_1 \phi_2). \quad (7)$$

For strong fields this can be approximated as

$$A\sigma H \sim c\left(\frac{m_2}{\tau_2} - \frac{m_1}{\tau_1}\right) \Big/ eH. \quad (8)$$

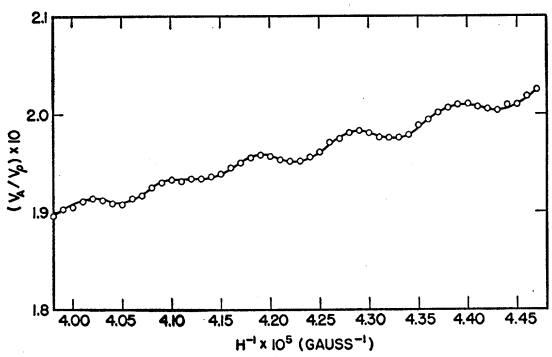

FIG. 11. The field dependence of the ratio of the Hall voltage to the resistance voltage for Sb IV at 1.57°K. H was parallel to the trigonal axis.

Here $A\sigma H$ is a linear function of H^{-1} provided m_2/τ_2 and m_1/τ_1 are field-independent. Since the mean value of $A\sigma H$ in Fig. 11 is a linear function of H^{-1}, we conclude, on the basis of this model, that $n_1 = n_2$ for antimony. However, the oscillatory behavior of $A\sigma H$ necessitates some adjustment to the above development. The simplest assumption one can make consistent with Eq. (8), is that the mobilities of the holes and electrons are oscillatory functions of the magnetic field. On a simple phenomenological development to explain the oscillations of A and σ one can make either the number of carriers and/or their mobilities periodic functions of H^{-1}. However, in the present analysis of the oscillations in $A\sigma H$, a changing number of carriers is of no significance since $n_1 = n_2$ and the numbers do not enter into the resulting expression, Eq. (8). Our conclusion is therefore, that at least the mobilities oscillate with H. Nothing can be said about the variation of n_1 and n_2 with H. A re-examination of the graphite[7] data in light of this analysis has shown that there too $A\sigma H$ undergoes oscillations which are periodic in H^{-1} and that the mean value is decreasing linearly with H^{-1}. Hence, $n_1 = n_2$ would also apply to the case of graphite. The model suggested here differs from that of Levinger and Grimsal[14] in that they attribute the Hall effect oscillations only to a changing number of electrons.

TABLE I. Temperature dependence of electrical resistance of antimony single crystals for $H = 0$. $r_t = \rho_t/\rho_{273°K}$. ϕ = angle between trigonal axis and electric current. ψ = angle between a binary axis and electric current.

$r_{78°K}$	$r_{4.2°K}$	ϕ	ψ	Crystal reference
0.187	0.014	90°	15° (or 75°)	Present data Sb IV
0.188	...	86.3°	88° (or 28°)	Rausch[a] $S_9{}^x$
0.260[b]	0.0791	?	?	McLennan *et al.*[c]

[a] See reference 11.
[b] At 82°K.
[c] See reference 15.

There is one additional feature of Eq. (7) which needs discussion. At $\phi_1 \phi_2 = 1$, $A\sigma H$ should exhibit a maximum. Over the range of field shown in Fig. 11 there is no such maximum. Actually, measurements were continued down to 6 kilogauss for this crystal, but $A\sigma H$ was still increasing with decreasing field.

(C) Temperature and Field Dependence of the Resistance

Table I gives the temperature dependence of the resistance of antimony single crystals for $H = 0$. Besides the present data (Sb IV), there are given comparative data from Rausch[11] and McLennan, Niven, and Wilhelm.[15]

Over the range 6–25 kilogauss the field dependence of the nonoscillatory component of resistance at 4.21°K

[14] J. S. Levinger and E. G. Grimsal, Phys. Rev. **94**, 772 (1954).
[15] McLennan, Niven, and Wilhelm, Phil. Mag. **6**, 666 (1928).

is given by the relation

$$\Delta\rho/\rho_0 \propto H^{1.7}, \quad (9)$$

for H either parallel or perpendicular to the trigonal axis. It is noted here that the magnetoresistance of bismuth single crystals[1] has a field dependence very similar to that given by Eq. (9).

Nothing definitive can be said about the temperature or field dependence of the oscillatory component of the magnetoresistance. Figure 7 shows that there is a strong temperature dependence for at least that particular orientation, but for other directions there seems to be little change over the range 1.5°–4.2°K. A more detailed study is needed before any firm conclusions are drawn. There is one more point, however, that is worthy of note. It concerns the fact that the amplitude of the oscillations in magnetoresistance as obtained from the Hall probes is considerably greater (relative to the total resistance) than that obtained from the resistance probes. Specifically for Sb IV at 25 kilogauss and 1.57°K the oscillatory component was 0.3 percent of the total resistance from the Hall probes and only 0.15 percent from the resistance probes. Aside from that difference the two magnetoresistance curves are very similar. They both exhibit maxima and minima at very nearly the same values of H^{-1}. This sort of behavior was also noted by Berlincourt and Steele[7] in their work on graphite. A possible explanation offered there was that the portion of the crystal between the Hall probes may have been purer (both from the single crystal and chemical points of view) than that between the resistance probes.

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Energy Levels of a Crystal Modified by Alloying or by Pressure

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A perturbation method of calculating the energy levels of a crystal modified by alloying or by pressure is studied. Initially the calculation is developed by means of conventional first-order perturbation theory. It is then shown what is wrong with this approach and how the calculation can be improved by a modified form of perturbation theory. It is further shown that this modified form of perturbation theory is particularly appropriate to cases where the unperturbed wave functions are expanded in terms of orthogonalized plane waves.

I. INTRODUCTION

WE wish to calculate the electronic energy levels of a crystal modified in a certain fashion from a knowledge of the one-electron wave functions and energy levels of the original unmodified crystal. In particular, we consider the modifications of the crystal (a) under hydrostatic pressure and (b) containing a small mole-percentage of a foreign atom placed in the crystal at random. In the following sections we will work out the general theory for a binary disordered alloy containing a small percentage of one constituent. It will then be seen that the results can be applied as a special case to the problem of the pure crystal under pressure. In Sec. II we will develop the theory by means of conventional first-order perturbation theory. In Sec. III, we will discuss what is wrong with this approach and how our theory can be improved by using a modified form of perturbation theory. In Sec. IV, we show how the results of Sec. III can be written in a particularly simple form by expanding our unperturbed wave functions in terms of orthogonalized plane waves.[1] The special case of a crystal of the diamond structure is worked out in detail. This case is particularly appropriate since the three most important examples of this crystal structure, namely diamond,[2] silicon,[3] and germanium,[4] have all been studied by the orthogonalized plane wave method.

Insofar as it deals with disordered alloys, this paper is intended to supplement a general discussion of the problem in a previous publication by the author.[5] Unlike the previous publication, however, here we will study the formal mathematical aspects of a method suitable for numerical calculations of specific physical systems. In fact, the present study was undertaken with the purpose in mind of forming a basis for a program of detailed numerical calculations on the germanium-silicon alloy and on germanium under hydrostatic

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