Electrical Conduction in Magnesium Stannide at Low Temperatures*

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Measurements of conductivity, Hall effect, and magnetoresistance of magnesium stannide at temperatures between 2 and 80°K indicate that this compound shows an "anomalous" behavior similar to that observed in germanium and other semiconductors. Results in the helium range suggest that the conduction takes place in a surface layer rather than in the bulk of the sample (impurity band conduction). Values of the density of surface carriers and their mobility are consistent with this theory.

INTRODUCTION

IN 1950, Hung and Gliessman[1] discovered an anomalous behavior of germanium at low temperatures. Measurements of the Hall coefficient R below 78°K indicated that this quantity does not increase indefinitely with decreasing temperature; instead, the curve of $\ln R$ *vs* $1/T$ shows a maximum in the range between 5 and 80°K depending on the impurity content. The conductivity decreases between 80°K and the temperature of the Hall maximum with a constant slope (which is related to the activation energy of the inherent impurity); however, at a temperature corresponding to the Hall maximum, ρ flattens off and increases with a much smaller slope towards lower temperatures.

Hung[2] suggested an explanation which is based on the concept of impurity band conduction; the assumption is that the wave functions of neighboring impurities show enough overlap to form an impurity band. The carriers would then have the possibility of moving in this band although with a much smaller mobility than in the conduction or valence bands.

In recent years several workers[3] have tried to put a theoretical foundation under Hung's hypothesis, but the details of this conduction mechanism are still poorly understood. Also, the amount of experimental data on the resistivity and Hall effect of germanium at low temperatures has been considerably extended.[4] Samples of Ge containing a wide range of impurities have been investigated systematically, the impurities being Ga, In, and Sb. Measurements on other semiconductors (InSb, TiO_2)[5] indicate that the behavior described above is not a specific property of germanium. These studies, however, far from clarifying the mechanism, have added new features which are difficult to explain.

In the hope that an investigation of yet another semiconductor might shed some light on this anomalous effect, the present work was undertaken. This paper presents measurements of conductivity, Hall effect and magnetoresistance of Mg_2Sn at temperatures between 2 and 78°K. (The properties of this semiconductor at higher temperatures have been discussed in a previous paper.[6])

It appears that the behavior of Mg_2Sn in the helium range can be explained on the basis of surface conduction. At the temperature of 4.2°K the bulk conductivity becomes much smaller than the conductivity of the surface. This makes it possible to evaluate such quantities as the number of surface carriers and the surface mobility. These values are consistent with the proposed picture.

Even though this paper does not contribute greatly to a better insight in the theory of impurity band conduction, it opens new possibilities in the study of surface phenomena. It may also help to clarify a number of observations on other semiconductors at low temperatures, where surface conduction and impurity band conduction are competing processes.

EXPERIMENTAL

Crystals of Mg_2Sn were grown by the Kyropoulos technique. Ingots prepared from commercial Mg and Sn were always n type. Addition of Sb made the crystals more n type. Adding small amounts of Ag, Au, and Cu produced p-type Mg_2Sn. It was impossible to influence the properties of the crystal by addition of Mg or Sn, indicating a very high degree of stoichiometry. In order to obtain samples of higher purity a number of crystals were zone-melted. Results show that the impurity content is not decreased by this process. It is possible that the magnesium reacts with the Vycor envelope and introduces new impurities in the melt. Spectroscopic analysis showed that several elements were present in very small amounts, but it is difficult to decide which of these is the dominant impurity.

The size of the samples used was about $10\times2\times1$ mm^3; surfaces were ground with 600-carborundum. One sample was cut to size by cleaving. (Etching with the

* Research supported by the Office of Naval Research.
[1] C. S. Hung and J. R. Gliessman, Phys. Rev. **79**, 726 (1950); **96**, 1226 (1954).
[2] C. S. Hung, Phys. Rev. **79**, 727 (1950).
[3] G. W. Castellan and F. Seitz in *Semiconducting Materials* (Butterworths Scientific Publications, London, 1951), p. 8; H. M. James and A. S. Ginzburg, J. Chem. Phys. **57**, 840 (1953); C. Erginsoy, Phys. Rev. **80**, 1104 (1950); X. Baltensperger, Phil. Mag. **44**, 1355 (1953).
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[6] Blunt, Frederikse, and Hosler, Phys. Rev. **100**, 663 (1955).

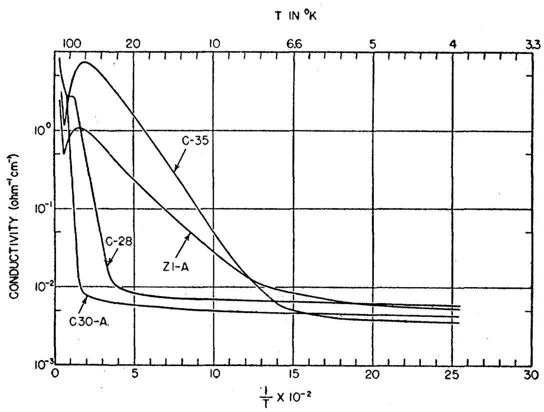

FIG. 1. Conductivity of p-type Mg_2Sn.

usual aqueous solutions was impossible due to the fact that Mg_2Sn corrodes rather easily.[6])

For electrical measurements specimens are mounted on a copper block, insulated from the copper by means of a thin mica sheet. This block is surrounded by a radiation shield and suspended by a nylon rod. The whole assembly is enclosed in a brass can, which can be either evacuated or filled with a low pressure of helium gas. For low temperature measurements the apparatus is immersed in liquid helium. A heater wound on the copper block enables one to cover the temperature range between 4.2°K and about 80°K. Conductivities, Hall coefficients, and magnetoresistive effects are measured by using a conventional dc method. The sample holder can be rotated through 360°, which makes it possible to investigate both transverse and longitudinal magnetoresistance.

RESULTS

Results of measurements of conductivity and Hall coefficient are shown in Figs. 1–4. Most of the Hall effect data were obtained in a field of 5000 oersteds. Sample Z3–A was also measured in a magnetic field of 360 oersteds; no appreciable difference in the Hall coefficient was found. The dependence on primary current was investigated; the behavior was strictly ohmic for all currents used. Sample Z3–B was measured twice; first with cleaved and then with ground surfaces. The results for these two cases are shown in Fig. 5.

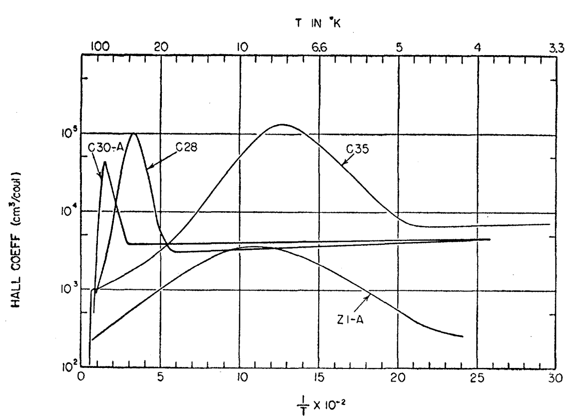

FIG. 2. Hall coefficient of p-type Mg_2Sn.

The magnetoresistance of several samples was determined as a function of magnetic field at 78°K and at 4°K. Some results of these measurements are given in Figs. 6 and 7.

Some of the important values deduced from the Hall and conductivity data are summarized in Table I. Column 4 gives the net concentration of impurities N_D-N_A (N_D=donor concentration, N_A=acceptor concentration), calculated from the Hall coefficient in the extrinsic range. We have attempted to calculate the absolute number of n- and p-type impurities using the law of mass action (for n type)[7]:

$$(n+N_A)(n+K_e)=N_DK_e, \qquad (1)$$

where n=electron concentration and $K_e=(2\pi m_ekT/h^2)^{\frac{3}{2}} \times\exp(-E_D/kT)$=equilibrium constant. (A similar law holds for holes.) The results of this calculation, however, appeared to be unreasonable.

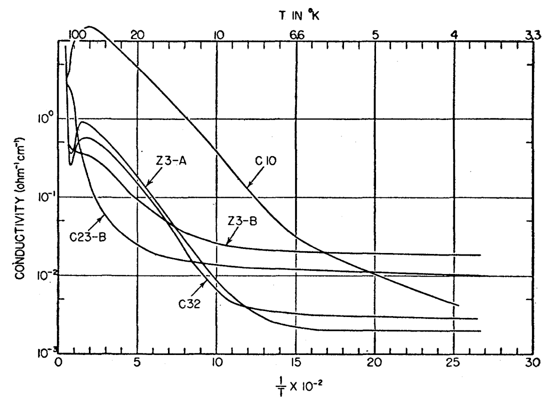

FIG. 3. Conductivity of n-type Mg_2Sn.

There are indications that two or more impurity levels are involved, which makes the application of Eq. (1) questionable. Also, the results will become very inaccurate when N_A (or N_D)$\gg|N_D-N_A|$. Calculation of the absolute concentrations N_D and N_A from the Brooks-Herring formula[8] for impurity scattering were not successful either.

The impurity activation energies in column 6 were deduced from the slope of $\ln(RT^{\frac{3}{2}})$ *vs* $1/T$.[9]

DISCUSSION

Conductivity and Hall Effect

It is clear from Figs. 1–4 that the temperature dependence of Mg_2Sn is very similar to that of germanium

[7] G. L. Pearson and J. Bardeen, Phys. Rev. **75**, 865 (1949).
[8] P. P. Debye and E. M. Conwell, Phys. Rev. **93**, 693 (1954).
[9] W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950), p. 472.

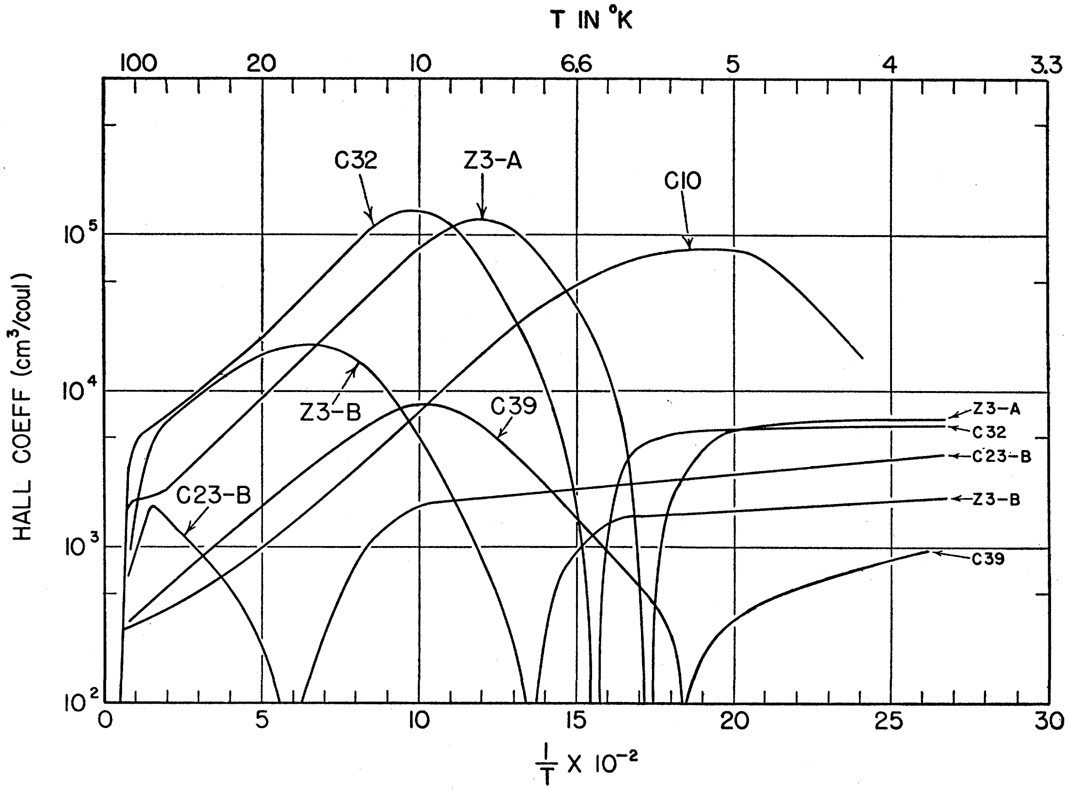

FIG. 4. Hall coefficient of n-type Mg_2Sn.

and p-type InSb. There are, however, some additional features:

(1) All n-type samples (except C10)[10] show a low-temperature reversal in the Hall coefficient.

(2) The Hall coefficients of all samples (except Z1–A) approach a value between 4000 and 8000 cm^3/coul at very low temperatures ($<4.2°K$) independent of their extrinsic Hall values (200–5000 cm^3/coul).

(3) The mobility $R\sigma$ of all samples (except Z1–A) attains comparable values (12–36 cm^2/volt-sec) in the helium range.

It is difficult to reconcile these characteristics with the mechanism of conduction in impurity levels. According to the principle of acceptor-donor compensation, all acceptor levels would always be filled in an n-type sample and vice versa for p-type specimens. On the other hand, the three points mentioned above would seem to indicate that one particular p-type impurity, which is present in all ground samples in about the same amount, is responsible for the low-temperature behavior.

The reported observations become understandable, however, if we assume that the p-type conduction is due to holes at the surface. The formation of such a p-type layer can easily be explained. The surface of an Mg_2Sn sample will be covered by a chemically or physically adsorbed oxygen film. This film is negatively ionized and will give rise to a positive space charge at the surface of the Mg_2Sn crystal. Such a situation has been described earlier by several workers for the cases of Ge and Si [11] and a few other materials.[12] However, these effects were observed at higher temperatures

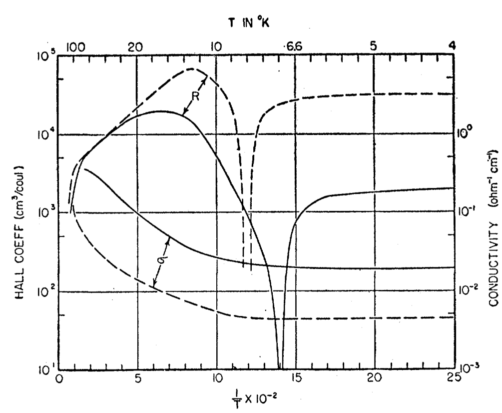

FIG. 5. Hall coefficient and conductivity of sample Z3–B (n type). —— ground surfaces; - - - - cleaved surfaces.

[10] Unfortunately, sample C10 broke before measurements below 4.2°K were taken.

[11] J. Bardeen, Phys. Rev. **71**, 717 (1947); J. Bardeen and S. R. Morrison, Physica **20**, 873 (1954); W. H. Brattain and C. G. B. Garrett, Physica **20**, 885 (1954); W. L. Brown, Phys. Rev. **91**, 518 (1953).

[12] D. J. M. Bevan and J. S. Anderson, Discussions Faraday Soc. **8**, 238 (1950), (ZnO); Garner, Gray, and Stone, Discussions Faraday Soc. **8**, 246 (1950), (Cu_2O).

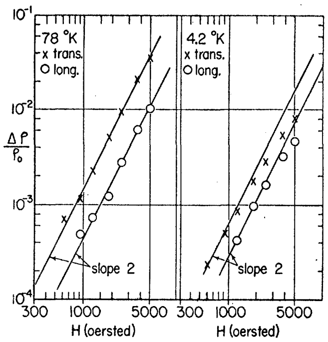

FIG. 6. Magnetoresistance of sample C35 (p type).

where the surface conductivity is small compared with the conductivity of the bulk material.

The formation of a p-type layer at the surface of an n-type crystal can be represented by a raising of the energy levels as indicated in Fig. 8(a). If the surface charge density is high (or the donor density low) a degenerate situation will occur [Fig. 8(b)]. The energy level diagram in the case of a p-type surface layer on a p-type crystal is given in Fig. 8(c).

Several workers[11] have shown that the rise of the energy bands at the surface (V_B) can easily be as much as a few tenths of an electron volt. This gives rise to appreciable effects, especially in small energy gap materials like Mg_2Sn.

That these assumptions are in agreement with the observations can be seen from a comparison with Figs. 2 and 4. The Hall coefficients of the purer n-type samples, C32 and Z3–A, and the p-type samples C35, C28, and C30–A, are practically flat in the helium range, while the n-type samples with larger impurity content show a small but definite slope of the Hall coefficient at low temperatures. It is possible that sample Z1–A is so impure that impurity band conduction predominates over surface conduction.

The strongest argument for the existence of surface conduction is the large difference in Hall coefficients measured with cleaved or ground surfaces (sample Z3–B, Fig. 5). The experience is that the ground surface oxidizes faster than the cleaved surface. Besides that, the surface area of the ground sample might be considerably higher than that of the cleaved specimen.[13] One would therefore expect a higher surface charge on the ground surface and consequently a smaller Hall coefficient. Small differences between ground samples might be due to different surface areas or slightly different surface conditions.

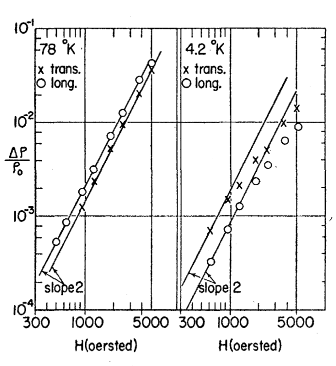

FIG. 7. Magnetoresistance of sample C32 (n type).

From the Hall coefficient and the conductivity one can—under certain assumptions—calculate the density of the surface carriers and their mobility. The results appear to strengthen the picture developed previously.

For this purpose we define a surface Hall coefficient R_s (cm²/coul)—corresponding to a surface density n (cm^{-2})—and a surface conductivity σ_s (coul/volt-sec). For the sake of simplicity we will assume that the surface conduction takes place mainly on the top and bottom surface implying that the thickness is small compared with the width of the sample. The Hall-emf is then given by $E_H = R_s \times I_s \times H$, and R_s is obtained by dividing the conventional R by t (see Fig. 9). The surface mobility μ_s appears to have the same value as μ: $\mu_s = R_s\sigma_s = R\sigma$.

TABLE I. Properties of Mg_2Sn samples at low temperatures.

Sample	Doping agent	R_{ex} cm³/coul	$N_D - N_A$ cm^{-3}	$R_{4.2}$ cm³/coul	ϵ (ev)	$(R\sigma)$ cm²/volt-sec
			n-type samples			
C10	···	320	2.3×10^{16}	···	0.003	···
C23–B	(Au)	~ 600	~1.2×10^{16}	3400	0.03	36
Z3–B	···	>1000	<7×10^{15}	1900	0.003	36
Z3–A	···	2100	3.5×10^{15}	6400	0.003	12
C32	···	5000	1.5×10^{15}	6000	0.003	17
C39	Sb	300	2.5×10^{16}	700 (4°K) 4700 (2°K)	0.003	7 (4°K) 25 (2°K)
			p-type samples			
C30–A	Au	~ 200	3.5×10^{16}	4500	(0.03)	19
Z1–A	···	220	3.4×10^{16}	270	0.003⁵	1.4
C28	Au	~1000	7.5×10^{15}	4400	0.015	26
C35	Cu	1050	7.0×10^{15}	6800	0.003⁵	38

Applying this to our data, we find, e.g., for sample C32: $R_s = 6000/0.114 = 54\,000$ cm²/coul and $n_s = 1.5 \times 10^{14}$ cm^{-2}. This indicates that the p-type surface layer is only one atom thick as can be shown by the following calculation. The average distance between atoms in an Mg_2Sn lattice is about 5 A. This corresponds to 4×10^{14} atoms per cm², which is of the same order of magnitude as n_s. This result is quite plausible, considering that the adsorbed oxygen layer is probably a monolayer.

On this basis one expects the mean free path of the carriers to be constant and of the order of 5 A. In this case

$$\tau = l/\bar{v}$$

[13] The question if the adsorption is chemical or physical is difficult to answer. On the one hand, it has been observed that Mg_2Sn is attacked by oxygen if water or water vapor is present. Considering the short time of handling and the mounting in vacuum, it is possible that this process has not advanced beyond 1 or 2 layers. On the other hand, one should not exclude the possibility of mere physical adsorption. In this case, one would expect that the samples in vacuum are covered only by a monolayer.

and

$$\mu = e\tau/m^* = 4el/3(2\pi m^* kT)^{\frac{1}{2}}.$$

For $T = 4.2°K$, $m^* = m_e$,[6] this yields a value for μ of 56 cm^2/volt-sec, which is of the same order of magnitude as the values of $(R\sigma)_{4.2}$ quoted in the last column of Table I.

We can estimate the mobility also in the following way. The Hall coefficient is given by[4]

$$R_H = -\frac{1}{e}\frac{r_c n_c \mu_c^2 - r_s n_s \mu_s^2}{(n_c\mu_c + n_s\mu_s)^2},$$

where n_c and n_s are, respectively, the absolute number of carriers in the conduction band and at the surface, μ_c and μ_s their mobilities, and r_c and r_s factors of the order of unity. One can easily show that at the maximum of the Hall coefficient,

$$n_c\mu_c = n_s\mu_s \quad (\text{if } \mu_c \gg \mu_s).$$

Calculating the surface mobility from this equation, one

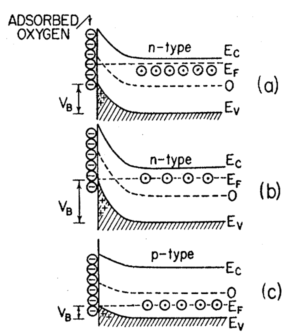

FIG. 8. Energy level diagrams at the surface of an Mg_2Sn sample.

finds for sample C32: $\mu_s = 15$ cm^2/volt-sec in good agreement with the value of $R\sigma$ (17 cm^2/volt-sec; see Table I).

Magnetoresistance

Figures 6 and 7 show two important features:

(1) The magnetoresistivity at 4.2°K is of the same order of magnitude as at 78°K.

(2) $\Delta\rho/\rho_0$ is certainly not proportional to H^2 at 4.2°K; for most samples the dependence on H is much closer to linear (above 1500 oersted).

The mobility calculated on the basis of the conventional semiconductor theory[14] yields values of the order of several thousands (cm^2/volt-sec). This is obviously in disagreement with the results from Hall and conductivity measurements. Even assuming mobilities of this order of magnitude, one would not expect to observe deviations from the H^2 behavior at fields as low as 1000 oersted.

Considering the conclusions reached in the previous section, it seems logical that the magnetoresistive effects at low temperatures are also related to the surface

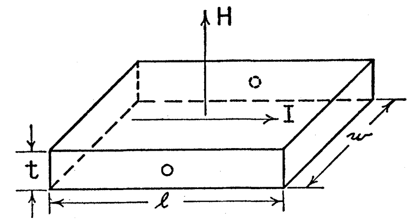

FIG. 9. Sample geometry for Hall measurement.

conduction. Therefore the question to be answered is: How will a magnetic field influence the conduction of degenerate carriers in a layer of several A thickness? A treatment of this problem is virtually nonexistent in the literature. Some help might be obtained from a paper by Sondheimer[15] who has treated magnetic effects (both longitudinal and transversal) in thin conductors (wires and films). The result of his calculation for the transverse magnetoresistance ($H \perp I$ and $\perp$ plane of film) is rather complicated. The expression for σ_0/σ_H contains three parameters: $\kappa = a/l$ (a being the thickness of the film and l the mean free path in bulk), $\beta = a/r_0$ (where $r_0 = m\bar{v}c/eH$), and p (a parameter describing the scattering mechanism of the electrons at the boundaries of the film). According to this expression, σ_0/σ_H increases very slowly for small H, then rises more rapidly and shows an oscillatory behavior for large magnetic fields. The first maximum is reached when β is approximately unity. The prediction for thin wires is that the resistance will decrease with H. (Such a behavior has been observed by MacDonald[16] in the case of sodium wires.) This theory also indicates that the magnetoresistive effects are considerably larger than in the bulk material.

We have discussed Sondheimer's treatment here to show that there is some analogy between his theoretical conclusions (partly confirmed by measurements[16]) and our observations. Similar experimental results have been obtained recently on InSb.[5]

This discussion of the magnetoresistive effects of Mg_2Sn is hardly more than an exposé of the problem. It is clear that a much deeper investigation, both experimental and theoretical, is urgently needed.

CONCLUSIONS

The galvanomagnetic effects of Mg_2Sn between 78°K and 10°K show a temperature dependence similar to that of germanium and InSb. The behavior in the helium range, however, can be explained on the basis of surface conduction rather than conduction in impurity levels. The results indicate that the carriers conduct in a monoatomic layer with a mobility about 50–100 times smaller than that of a bulk crystal. Such a layer is easily produced due to adsorption of oxygen on the surface. These measurements have shown that an

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[15] E. H. Sondheimer, Advances in Phys. **1**, 1 (1952).

[16] D. K. C. MacDonald, Nature (London) **163**, 637 (1950); Proc. Phys. Soc. (London) **A63**, 290 (1950). D. K. C. MacDonald and K. Sarginson, Proc. Roy. Soc. (London) **A203**, 223 (1950).

investigation of the galvanomagnetic effects at very low temperatures provides a powerful tool to obtain information about surface properties of semiconductors. For very thin specimens or films, surface conduction may already be important at much higher temperatures.

ACKNOWLEDGMENTS

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Study of 1/*f* Noise in Semiconductor Filaments*

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A theory is devised for the generation of 1/*f* noise in semiconductor filaments, involving the diffusion of impurity atoms along the surface of the sample and along edge dislocations within the bulk. A set of six experiments is described which tends to corroborate this theory.

I. INTRODUCTION

ASSUMING that 1/*f* noise in semiconductor filaments is a result of a fluctuation in the sample resistance, it has been possible to construct a logically consistent theory which can explain at least the more obvious empirical features of the noise generating process. Moreover, a set of six experiments (most of which had been suggested from an inspection of the theory) were performed and produced data which, when analyzed, tended to corroborate the theory.

It is felt by the author, that the combined theoretical and experimental study has now developed to the point where a detailed description is justified. This description will, therefore, be presented in the following sections.

II. THEORY

1. Preliminary Considerations

Before the presentation of a specific theory, a general requirement for any 1/*f* noise mechanism will be pointed out. This will be used later to restrict the number of possible noise models. The observed 1/*f* spectrum in semiconductor noise can most probably be accounted for by a process which consists of a large number of independent events. For a constant impressed voltage, the occurrence of each event produces a small change in the flow of current, whose endurance will be the same as the lifetime of the event. The events must then have a very wide range of lifetimes, some extending as long as several hours. One test, therefore, of any suggested noise-generating mechanism is its ability to produce single events causing current changes of very long duration (of the order of hours). Two possible noise models proposed in the past appear to fail this test.

The first is a simple trapping process under the condition of quasi-equilibrium (i.e., where the Fermi levels for holes and electrons are equal) such as considered by van der Ziel.[1] Here a single mobile carrier (either hole or electron) is trapped, for a time depending on the energy depth of the trap involved, and then released. A wide range of trapping times, T, is implicit in the assumption of a spectrum (or band) or energy depths. This type of mechanism, however, cannot give rise to a 1/*f* spectrum, since no single trapping event can cause a current change of long duration. If T is assumed to be a very long time, it would be necessary for the current to be decreased as long as the mobile carrier is trapped. This situation is illustrated in Fig. 1(a). Actually, however, the current alteration caused by the trapping event will be as shown in Fig. 1(b). The reason for this is that a mobile carrier can give rise to current for only as long as it is free. Moreover, when a carrier is trapped for a time T, it can have been in existence only for a time τ (the lifetime of the carrier) before it was trapped, and live only a time τ after it has been released. Since in actual semiconductors $\tau \ll T$, the contribution to the current from the single carrier as a result of being trapped must be as shown in Fig. 1(b). There will effectively be two short positive pulses of duration τ instead of one long negative one of duration T. Thus, in this process, a single event is not capable of producing a conductivity change of long duration and is, as a result, insufficient to account for the shape of the low-frequency end of the 1/*f* spectrum. Apparently, then, a simple trapping process cannot produce 1/*f* noise.

The second type of noise mechanism is a simple modulation of the generation of decay rate of either

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[1] A. van der Ziel, Physica 16, 359 (1950).