JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 22, No. 3, MARCH, 1967

Electric Conduction in Phosphorus Doped Silicon at Low Temperatures

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(Received December 2, 1966)

The impurity conduction in phosphorus doped *n*-type silicon has been investigated at temperatures between 1.1°K and 300°K. The samples ranged in concentration of excess donors from $1.2.10^{18}$ to $2.5.10^{20}$cm^{-3}. A metallic type impurity conduction and a negative magnetoresistance are observed in samples containing higher than 4.10^{18}cm^{-3} excess donors. An intermediate type impurity conduction is observed in samples containing from $1.7.10^{18}$ to 4.10^{18}cm^{-3} excess donors. In metallic samples with donor concentration higher than 6.10^{18}cm^{-3}, the resistivity increases monotonically with temperature T up to the Fermi degeneracy temperature T_D of respective samples according to a simple formula, $\rho(T)=\rho(4.2°\text{K})[1+A(T/T_D)^B]$, where A and B are constants.

§ 1. Introduction

Previous investigations by Swartz[1] and by Ray and Fan[2] have shown that the impurity conduction of low and intermediate concentration types in silicon is quite similar to those observed in germanium.[3] A magnetoresistance study on *n*-type silicon carried out by Tufte and Stelger[4] covered a very wide range of phosphorus concentration, *i.e.* from 10^{15} to 10^{20} cm^{-3}. Their measurement at 4.2°K revealed that a metallic type impurity conduction takes place in samples containing higher than 4.10^{18}cm^{-3} excess donors. Negative magnetoresistance is observed in samples of the metallic region at 4.2°K,[4–6] while in less doped samples the magnetoresistance is positive.[1,2,4] These magnetoresistance features are also resemblant to those observed in *n*-type germanium.[7–9]

The present work was undertaken primarily to supply well characterized phosphorus doped silicon crystals for ESR experiment.[10] Because of a special interest in the relation between the negative magnetoresistance and the electron paramagnetic resonance, detailed experiments have been carried out of the magnetoresistance effect in these crystals. Results of these experiments are described in comparison with those in *n*-type germanium. A mention is also given of the temperature dependence of the resistivity in the metallic samples because of recent interests in this problem.[11–13]

§ 2. Experimental Details

Single crystals of silicon containing between 2.10^{18} to 2.10^{20} cm^{-3} phosphorus atoms were supplied by Chisso Corporation. Samples were cut from the crystals in such a way as to give the best possible homogeneity of concentration, but no attempt was made to prepare the samples with any particular crystallographic orientation. Most of the samples were about $0.1\times0.1\times0.7$cm^3 in dimension. No particular surface treatment was done. Ohmic electrical contacts were formed by alloying 0.08mmϕ gold wire doped with 0.08 per cent antimony.

The electric field applied to the sample was kept below 30 mV/cm, and dc voltages of 0.1 microvolt to 9.9999 mV were read on a digital voltmeter and were punched out on a paper tape for computer.

Magnetic fields up to 50kOe were provided by a superconducting solenoid. The field strength was measured by the magnetoresistance of a piece of copper wire. For measurements above 4.2°K, magnetic fields up to 20kOe were applied by an electromagnet.

Temperatures between 4.2°K and 300°K were measured by a platinum resistance thermometer, and below 4.2°K by the vapor pressure of liquid helium. Temperatures between 4.2°K and 77°K were attained by placing the sample above the liquid helium bath and regulating the flow of cold helium gas against the heat inputs from outside radiation and an electric heater. By using liquid nitrogen instead of liquid helium, temperatures above 77°K were attained.

The samples investigated are listed in Table I, together with their excess donor concentra-

Table I.

Code No.	N_D-N_A (cm^{-3})	$\rho_{300°K}$ (ohmcm)	$\rho_{77°K}$ (ohmcm)	$-R_{H\,77°K}$ (cm^3/C)	$\rho_{4.2°K}$ (ohmcm)	$-R_{H\,4.2°K}$ (cm^3/C)
0	1.21 10^{18}	1.64 10^{-2}	6.81 10^{-2}	6.81 10^{+1}		
1	1.60 〃	1.55 〃	5.79 〃	9.59 10^{0}		
2	1.75 〃	1.32 〃			9.78 10^{+3}	10^{4}
3	2.30 〃	1.24 〃	2.44 〃	2.91 〃	4.58 10^{-1}	6.8 10^{0}
4	2.55 〃	1.13 〃	2.19 〃	2.60 〃	3·42 〃	5.07 〃
5	2.69 〃	9.64 10^{-3}	1.73 〃	2.31 〃	1.08 〃	3.80 〃
6	2.81 〃	1.08 10^{-2}	1.84 〃	2.17 〃	7·46 10^{-2}	3.41 〃
7	2.81 〃	1.06 〃	1.78 〃	2.20 〃		
8	2.99 〃	9.56 10^{-3}	1.50 〃	2.03 〃		
9	3.11 〃	1.02 10^{-2}	1.73 〃	2.18 〃	2.31 〃	2.08 〃
10	3.15 〃	8.68 10^{-3}	1.29 〃	1.87 〃	1·98 〃	2.16 〃
11	3.59 〃	8.77 〃	1.10 〃	1.60 〃		
12	3.96 〃	8.80 〃			9.43 10^{-3}	1.51 〃
13	4.11 〃	8.19 〃	9.45 10^{-3}	1.40 〃	7.37 〃	1.40 〃
14	4.12 〃	9.04 〃	1.07 10^{-2}	1.40 〃	8.86 〃	1.32 〃
15	4.43 〃	9.82 〃	1.09 〃	1.31 〃	8.17 〃	1.31 〃
16	6.22 〃	7.55 〃	6.49 10^{-3}	9.41 10^{-1}	3.81 〃	8.85 10^{-1}
17	6.97 〃	7.70 〃	6.36 〃	8.48 〃	4.04 〃	7.94 〃
18	8.02 〃	6.15 〃	4.50 〃	7.52 〃	2.87 〃	6.84 〃
19	9.71 10^{19}	5.36 〃	3.44 〃	6.19 〃	2.30 〃	5.56 〃
20	1.10 〃	4.57 〃	2.87 〃	5.6 〃	1.92 〃	5.14 〃
21	1.47 〃	3.42 〃	1.95 〃	4.18 〃	1.41 〃	3.80 〃
22	1.50 〃	3.37 〃	1.98 〃	4.06 〃	1.42 〃	3.89 〃
23	2.28 〃	2.54 〃	1.13 〃	2.70 〃	1.07 〃	2.53 〃
24	2.35 〃	2.36 〃	1.12 〃	2.63 〃	9.76 10^{-4}	2.41 〃
25	2.42 〃	2.26 〃	1.17 〃	2.52 〃	9.42 〃	2.37 〃
26	2.53 〃	2.26 〃	1.19 〃	2.42 〃	9.64 〃	2.29 〃
27	2.75 〃	2.07 〃	1.07 〃	2.18 〃		
28	2.82 〃	2.15 〃				
29	3.24 〃	1.54 〃	9.07 10^{-4}	1.86 〃		
30	3.28 〃	1.88 〃	9.89 〃	1.88 〃		
31	3.28 〃	1.82 〃	9.39 〃	1·84 〃		
32	3.39 〃	1.74 〃	9·34 〃	1.73 〃		
33	3.58 〃	1.62 〃	8.51 〃	1.66 〃		
34	4.46 〃	1.35 〃	7.17 〃	1.78 〃	6.48 〃	1.22 〃
35	5.01 〃	1.39 〃	7.61 〃	1.32 〃		
36	5.86 〃	9.67 10^{-4}	5.52 〃	9.15 10^{-2}	4.93 〃	1.12 〃
37	8.02 〃	7.77 〃	4.55 〃	7.38 〃	4.20 〃	6.97 10^{-2}
38	9.52 〃	6.99 〃	4.03 〃	5.89 〃	3.17 〃	5.95 〃
39	9.93 〃	7.01 〃	4.23 〃	6.16 〃	3.98 〃	6.17 〃
40	1.20 10^{20}	7.87 〃	4.78 〃	3.58 〃		
41	1.23 〃	6.35 〃	3.89 〃	4.98 〃	3.61 〃	4.79 〃
42	1.39 〃	5.53 〃	3.52 〃	3.94 〃	3.52 〃	4.19 〃
43	1.40 〃	5.40 〃	3.37 〃	3.93 〃	3.25 〃	3.93 〃
44	2.23 〃	6.01 〃	3.97 〃	2.62 〃	3.83 〃	2.68 〃
45	2.50 〃	5.36 〃	4.29 〃	2.14 〃	4.13 〃	2.27 〃

tion N_D-N_A, resistivity ρ and Hall coefficient R_H. To determine R_H listed in the Table a magnetic field of 7 kOe was used. The excess donor concentration was estimated from the room temperature Hall coefficient using the relation $N_D-N_A=-1/R_He$, where $-e$ is the electron charge.

§ 3. Temperature Dependence of the Resistivity and Hall Coefficient

Figures 1 and 2 show the resistivity ρ and the Hall coefficient R_H for various samples as a function of temperature T. In these figures the vertical line attached on each curve represents the degeneracy temperature T_D for that sample. T_D was estimated from N_D-N_A assuming the cyclotron mass and six valleys. The use of the Hall concentration values for N_D-N_A needs a correction of T_D by 10 to 20 per cent for a detailed argument. The shapes of the resistivity and Hall coefficient curves are just similar to those reported previously.[11]

Figure 3 shows the relation between the Hall concentration at 4.2°K and that at 300°K. Two concentrations coincide well for samples with N_D-N_A higher than 4.10^{18} cm^{-3}. Below this concentration the Hall concentration at 4.2°K decreases steeply from that at 300°K. For samples with N_D-N_A higher than 4.10^{18} cm^{-3}, the Hall coefficient is nearly constant and the resistivity decreases slightly as T falls from T_D, while, for samples with N_D-N_A lower than 4.10^{18}cm^{-3}, as

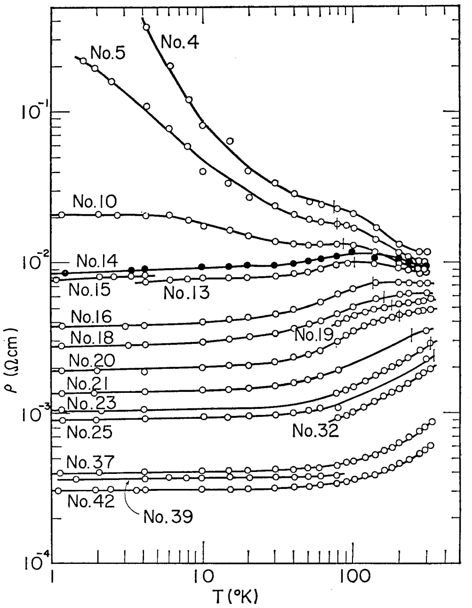


Fig. 1. Temperature dependence of the resistivity ρ. The vertical line attached on each curve represents the degeneracy temperature T_D.

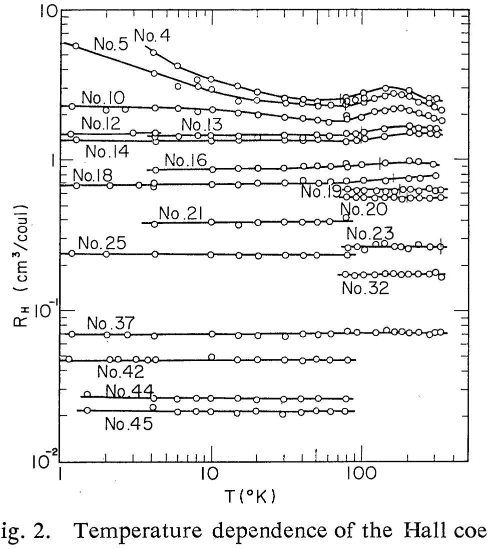


Fig. 2. Temperature dependence of the Hall coefficient R_H. The vertical lines show the degeneracy temperature.

will be shown in the next section, the Hall coefficient and the resistivity increases exponentially with $1/T$ at sufficiently low temperatures. These features suggest the boundary between the metallic and the intermediate regions of the impurity conduction at a Hall concentration of 4.10^{18} cm^{-3}.

For samples No. 0 and 1 the Hall effect was not detected at 4.2°K. Thus the range of the Hall concentration for the intermediate type impurity conduction is estimated to be from $1.7.10^{18}$ to $4.0.10^{18}$cm^{-3}. This range of the intermediate impurity conduction corresponds to the range of the relative mean distance $r_s \equiv (3/4\pi(N_D - N_A))^{1/3}/a^*_H$, where a^*_H is the effective Bohr radius of the donor electron, between excess donors from 2.3 to 3.1. This range is in good agreement with that for antimony doped germanium from 2.4 to 3.3.

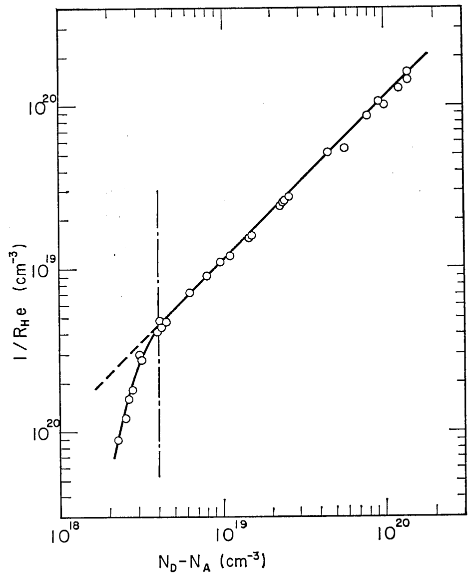


Fig. 3. The Hall concentration $-1/R_H e$ at 4.2°K versus $N_D - N_A$.

Figure 4 shows a representation of the temperature dependence of the resistivity for the metallic samples. The ordinate is the relative increase of the resistivity,

$$\Delta\rho/\rho(4.2) \equiv [\rho(T) - \rho(4.2°\text{K})]/\rho(4.2°\text{K}) ,$$

and the abscissa is the temperature normalized at T_D. This type of the plot was first made by Katz *et al.*[13] for n-type germanium doped heavily with antimony or arsenic. They found that the curves for samples with different concentration of carriers are represented by a simple formula,

$$\Delta\rho/\rho(4.2) = A(T/T_D)^B, \qquad (1)$$

and that the constants A and B depend only on the kind of the doped impurity irrespective of its concentration. In our case, though the experimental points are well alined on curves represented by (1), A and B depend on the concentration except for the two most heavily doped samples. As suggested by Katz *et al.*[13] the electron-electron intervalley scattering is undoubtedly a most important origin of the

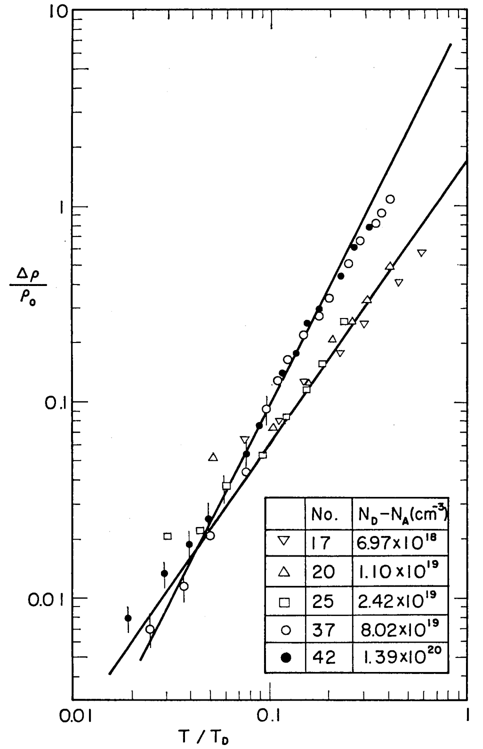
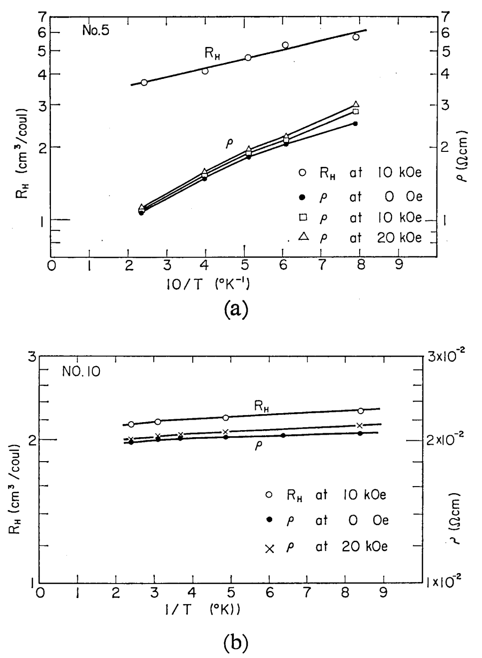


Fig. 4. Temperature dependence of the resistivity. The ordinale is $\Delta\rho/\rho(4.2) \equiv [\rho(T)-\rho(4.2°\mathrm{K})]/\rho(4.2°\mathrm{K})$ and the abscissa is T/T_D.

temperature dependent resistivity,and just explains the case of $B=2$ for arsenic doped germanium and for the two most heavily doped silicon samples. The magnitude of A for the most heavily doped silicon is 10, which is larger than that for arsenic doped germanium by a factor of 5. This may be partly due to the difference in the number of valleys. It has been known in n-type germanium that there exists another type of scattering, which is effective even under one valley condition, with a negative temperature coefficient.[14] A mixing of this type of scattering to the electron-electron intervalley scattering would make the constant B smaller. At present, no satisfactory explanation is found of this scattering with a negative temperature coefficient, and, thus, no reasonable explanation is given of the question why this scattering is effectively mixed only in antimony doped germanium and in less doped silicon.

§ 4. Magnetoresistance Effect in the Intermediate Region



(a)

(b)

Fig. 5. Temperature dependence of the resistivity and the Hall coefficient of intermediate type samples. (a) N_D-N_A: 2.69.10¹⁸cm⁻³ (b) N_D-N_A: 3.15.10¹⁸ cm⁻³

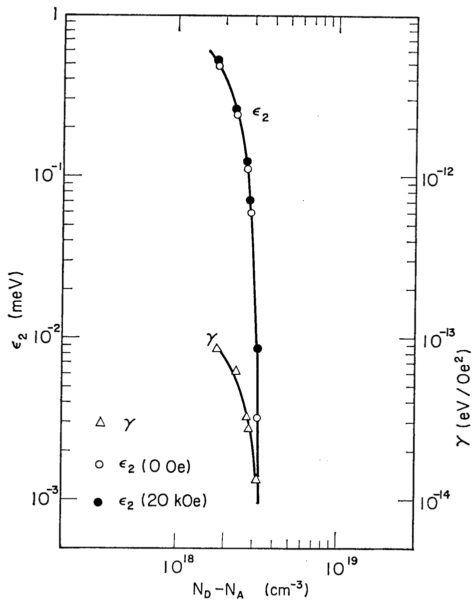


Fig. 6. The variation of ε_2 and γ with N_D-N_A.

Figure 5 shows the effect of the magnetic field H on the log ρ versus $1/T$ curves for two intermediate samples. The Hall coefficient R at a magnetic field of 10kOe is also shown in this figure. In Fig. 6 the slope ε_2 of the resistivity curve at the lowest temperatures and at zero and 20kOe is plotted against N_D-N_A. ε_2 decreses steeply with increasing N_D-N_A.

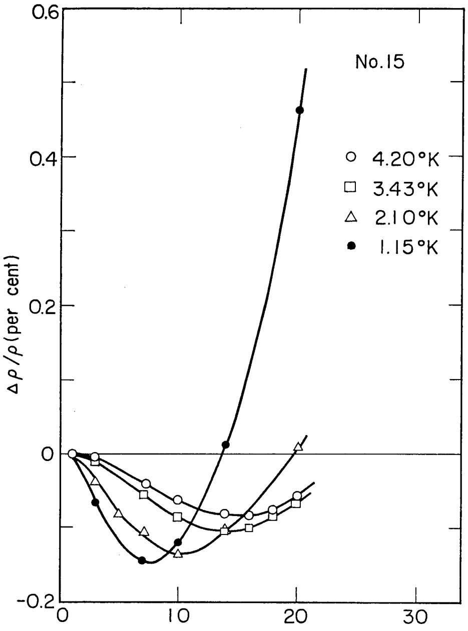
ε_2 increases with magnetic field with a dependence of

$$\varepsilon_2(H)=\varepsilon_2(0)+\gamma H^2\,, \qquad (2)$$

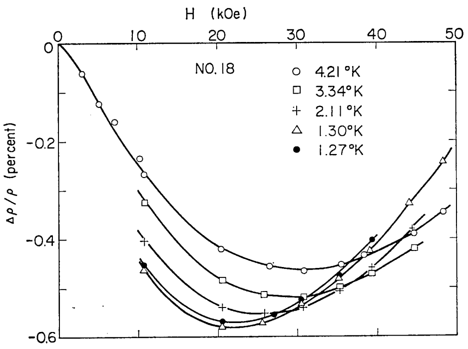
which is one of the remarkable characteristics of the intermediate concentration type impurity conduction.[7] The concentration dependence of γ is plotted in Fig. 6. The magnitude of γ for silicon is smaller than that for uncompensated germanium by about one order of magnitude, but is comparable to that for compensated germanium.[7]

§ 5. Magnetoresistance Effect in the Metallic Region

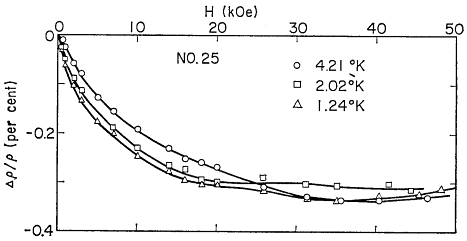
Figure 7 shows the magnetoresistive ratio $[\rho(H)-\rho(0)]/\rho(0)$ as a function of the magnetic field strength H for four representative metallic samples, *i.e.* those with N_D-N_A of $4.4.10^{18}$, $8.0.10^{18}$, $2.4.10^{19}$, and $1.39.10^{20}\text{cm}^{-3}$ respectively. The general feature is quite resemblant to that observed in *n*-type germanium. For the lower concentration samples the magnetoresistive ratio shows a minimum. The absolute value of the ratio at the minimum is larger at lower temperatures. The magnetic field strength of the minimum is lower for lower temperature, and is higher for samples of higher concentration. The ratio becomes positive at the highest magnetic fields for lower concentration samples. The minimum of the magnetoresistive ratio disappears for samples with concetration higher than 2.10^{19}cm^{-3} in the magnetic fields below 50kOe. For these samples the ratio becomes insensitive to the temperature in the high magnetic fields and a Shubnikov-de Haas like oscillation appears.



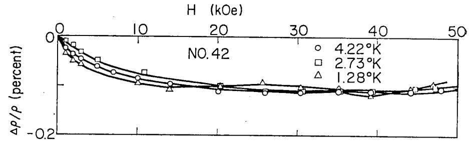
(a)



(b)



(c)



(d)

Fig. 7. Magnetoresistive ratio as a function of magnetic field strength.

(a) N_D-N_A: $4.43.10^{18}\text{cm}^{-3}$
(b) N_D-N_A: $8.02.10^{18}\text{cm}^{-3}$
(c) N_D-N_A: $2.42.10^{19}\text{cm}^{-3}$
(d) N_D-N_A: $1.39.10^{20}\text{cm}^{-3}$

In Fig. 8 the maximum absolute value of the magnetoresistive ratio at 1.2°K is shown as a function of N_D-N_A. Though the magnitude of the negative magnetoresistance effect becomes smaller with the increase of N_D-N_A, there is no indication of the disappearance of this effect, in contrary to a previous investigation.[6] In Fig. 8 the corresponding value of antimony doped *n*-type germanium[9] is also shown. The $-2/3$ power dependence is quite similar to silicon and germanium. The magnitude for silicon is smaller by a factor of about two compared to the extrapolation of the data for germanium. This

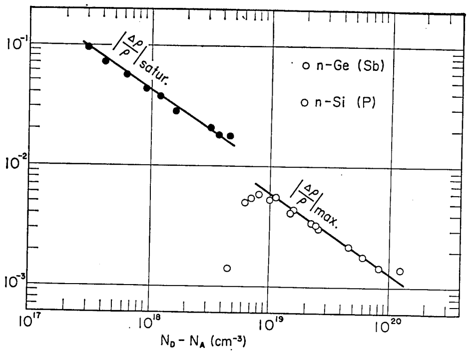


Fig. 8. The maximum absolute value of the magnetoresistive ratio at 1.2°K versus N_D-N_A.

magnitude for silicon as a function of r_s is smaller than that for germanium by one order of magnitude.

The magnetic field strengths of the magnetoresistive ratio minimum for silicon is much larger than that for germanium.[9]

Proposals have been made of the mechanism of the negative magnetoresistance effect in the metallic impurity conduction. Among these a picture[15] that a system of localized electrons appears in the random lattice of impurity atoms and that an *s-d* scattering of the conduction electrons by these localized electrons results in a negative magnetoresistance seems plausible for the case of *n*-type germanium and *n*-type silicon. An anomalous magnetic susceptibility has been observed in these silicon samples.[16,17] These observations suggest that there exsits a magnetic system in addition to a usual electron gas described by Landau-Peierls-Pauli theory. The magnetic behaviors of this additional system will be described in a forthcoming paper.[17]

Acknowledgements

The authors are grateful to S. Maekawa and H. Ue for supplying crystals used for this study. They appreciated stimulating discussions with S. Maekawa on the magnetic behaviors. Their heartfelt thanks are due to Professor M. Shibuya for the interests and encouragements through the course of the present work.

References

1) G. A. Swartz: J. Phys. Chem. Solids **12** (1960) 245.
2) R.K. Ray and H.Y. Fan: Phys. Rev. **121** (1961) 768.
3) H, Fritzsche: J. Phys. Chem. Solids **6** (1958) 69, including references.
4) O. N. Tufte and E. L. Stelger: Phys. Rev. **139** (1965) A265.
5) H. Roth, W. D. Straub, W. Bernard and J. E. Mulhern: Phys. Rev. Letters **11** (1963) 328.
6) M. Balkanski and A. Geismar: Solid State Commun. **4** (1966) 111.
7) C. Yamanouchi: J. Phys. Soc. Japan **18** (1963) 1775.
8) C. Yamanouchi: J. Phys. Soc. Japan **20** (1965) 1209.
9) W. Sasaki: J. Phys. Soc. Japan **20** (1965) 825, including references.
10) S. Maekawa and N. Kinoshita: J. Phys. Soc. Japan **20** (1965) 1447.
11) P.W. Chapman, O.N. Tufte, J. David Zook and Donald Long: J. appl. Phys. **34** (1963) 191.
12) Donald Long, J. David Zook, P. W. Chapman and O. N. Tufte: Solid State Commun. **12** (1964) 191.
13) M.J. Katz, S.H. Koenig and A.A. Lopez: Phys. Rev. Letters **15** (1965) 828.
14) Maurice J. Katz: Phys. Rev. **140** (1965) A1323.
15) Y. Toyozawa: J. Phys. Soc. Japan **17** (1962) 986.
16) S. Maekawa: *Proc. Int. Conf. Semiconductor Physics*, Kyoto (1966) p. 574.
17) W. Sasaki, S. Maekawa and J. Kinoshita: J. Phys. Soc. Japan 22 (1967) 928.