PROCEEDINGS OF THE INTERNATIONAL CONFERENCE ON THE PHYSICS OF SEMICONDUCTORS, KYOTO, 1966
JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 21, SUPPLEMENT, 1966

XIII-1. Negative Magnetoresistance in the Metallic Impurity Conduction

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A review is given of the negative magnetoresistance effect, which has been found in various semiconductors. The observed effect, together with related phenomena, is explained from a point of view that this anomalous effect is caused by a magnetic system which appears in the random lattice of impurity atoms in the semiconductor.

§ 1. Introduction

Experiments of the impurity conduction in semiconductors[1] revealed an important aspect of the conduction of electricity in an array of hydrogen-like atoms, that is, the transition from metallic to non-metallic state occurs when the density of atoms becomes low.[2] In the case of the array of impurity atoms in semiconductors, this transition is observed to occur at the concentration where the mean interatomic distance is about 2.5 times the effective Bohr radius. This is in good agreement with a crude estimation by Mott.[2] Our main interest is in semiconductors in the state of the metallic impurity conduction.

Experiments on the electronic properties in these semiconductors, such as resistivity,[1] galvanomagnetic effect,[1,3] piezoresistance,[4] specific heat,[5] and magnetic susceptibility,[6] have been explained fairly well by assuming that the conduction electrons form a degenerate Fermi gas with the same density of states mass as that of the conduction band electrons. A detailed examination of these experimental results, however, reveals that non of these, except for piezoresistance, can be satisfactorily explained by assuming only a degenerate Fermi gas. That is to say, i) the resistivity shows a conspicuous temperature dependence to below 1°K, ii) a negative or positive anomalous magnetoresistance is observed, iii) a deviation from the degenerate gas value is observed in both specific heat and magnetic susceptibility. It is convinced that these deviations are essentially due to the randomness of the lattice of the impurity atoms in which these electrons are moving.

In this article we take up especially the negative magnetoresistance which seems to provide a clue to understand the features of the metallic impurity conduction mentioned above. An analogous phenomenon observed in Cu-Mn alloys[7] reminds us to interpret the negative magnetoresistance effect in semiconductors by introducing a system of localized electrons with magnetic moments embeded in the impurity lattice. This idea was first mentioned by Toyozawa, who showed its possibility based on a microscopic theory.[8] The randomness of the impurity lattice played an essential role in this theory. In the following sections tentatives are given to interpret the above mentioned deviations from the degenerate gas picture by introducing the localized magnetic moments. Section 2 deals with the typical negative magnetoresistance phenomena in *n*-type germanium, § 3 with the magnetic properties in *n*-type germanium and *n*-type silicon, § 4 with the temperature dependence of the resistivity in *n*-type germanium, and § 5 with the comparison of the magnitude of the negative magnetoresistance for various semiconductors. Through these tentatives it will be shown that the major part of the role of the randomness of the impurity lattice is represented by a system of the localized magnetic moments.

§ 2. Negative Magnetoresistance in *n*-type Germanium

Figure 1 shows a typical plot of the change of the resistivity as a function of the magnetic

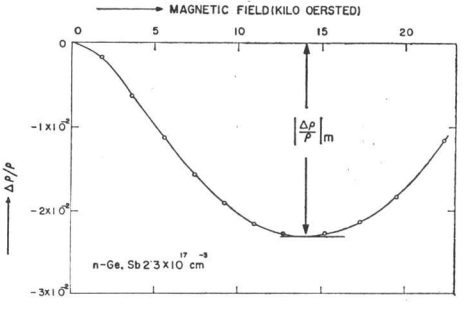

Fig. 1. The magnetoresistance ratio as a function of magnetic field strength.

field strength. The resistivity decreases quadratically in the lowest fields. Anisotropy consistent with the cubic symmetry is seen in these fields. The decrease of the resistivity becomes less steep as the field is increased, and saturates at a magnetic field. In the higher fields the resistivity begins to increase. The same plot as Fig. 1 with the abscissa H^2 instead of H shows that the curve tends towards a straight line of positive gradient in the highest fields. This positive gradient is independent of temperature and its magnitude is of the order of the square of the Hall mobility. Thus, it is supposed that the total magnetoresistance consists of two components. One is the usual positive component proportional to the square of the magnetic field, which predominates at higher fields. The other is the anomalous and temperature dependent component, which predominates in the lower fields and saturates at a field where the curve in Fig. 1 attains a maximum. Shubnikov-de Haas oscillation is seen in fields higher than 20 kϕ under favorable conditions.[9] In the following we are interested in the negative component.

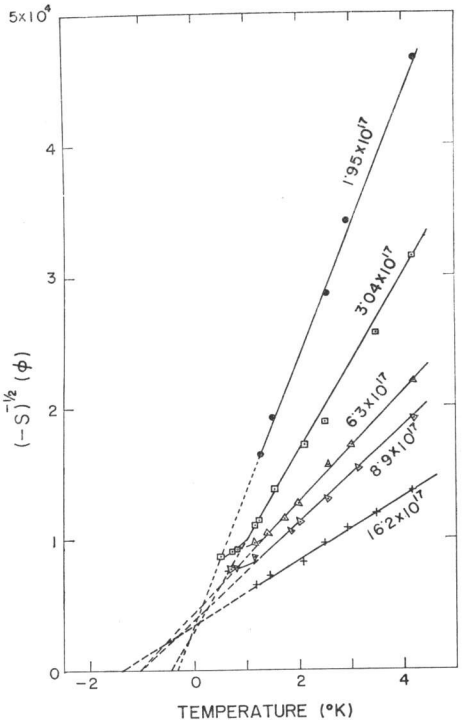

Fig. 2. The temperature dependence of low field magnetoresistance coefficient S. The ordinate is $(-S)^{-1/2}$. Figures indicate the concentration of antimony atoms. Straight lines correspond to Curie Weiss law.

The low field magnetoresistance coefficient S, defined by

$$S=\lim_{H\to 0} d(\Delta\rho/\rho)/d(H^2)\ ,$$

depends on temperature and the carrier concentration. Figure 2 shows a plot of the temperature dependence of S which reminds of the magnetic origin of this effect. In this figure the ordinate is $(-S)^{1/2}$ and the abscissa is the temperature. The straight line corresponds to a Curie Weiss law,

$$(-S)^{1/2}=\zeta/(T-\theta)\ .$$

This result is consistent with a picture that there exist localized magnetic moments, which obey a Curie Weiss law, and the magnetic scattering of the conduction electrons by these localized magnetic moments results in the negative magnetoresistance. The interaction between the localized magnetic moments, the existence of which is represented by the finite value of the paramagnetic Curie temperature θ, causes a deviation of the experimental points from the straight line near 1°K. The absolute value of θ increases with increasing carrier concentration.

Figure 3 shows a plot of the magnetoresistance of a sample at various temperatures as a function of $H/(T-\theta)$. Curves for different temperatures coincide each other to a fairly high field where the change is no longer quadratic. Better coincidence can be obtained when the normal component of the magnetoresistance is subtracted from each curve, which is indicated by closed symbols. It is seen that experimental points for various temperatures, after subtracting the normal component, are aligned on a single curve. This curve resembles to the Brillouin function, with $H/(T-\theta)$ variable, and suggesting that the negative component of the magnetoresistance is a function

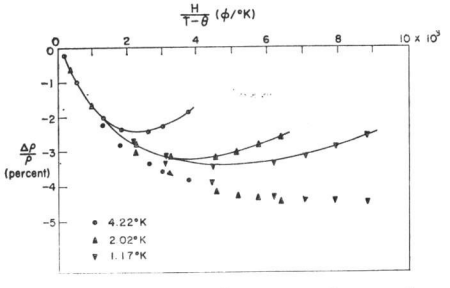

Fig. 3. The magnetoresistance ratio as a function of $H/(T-\theta)$, where θ is the paramagnetic Curie temperature estimated from the plot of Fig. 2. Closed symbols represent the negative component.

of the magnetization of the localized magnetic moments. The saturation of the decrease of the resistivity corresponds to the saturation of the magnetization of the localized magnetic moments. The magnitude of the saturation field suggests a rather large value for the effective Bohr magneton of the localized moments. Figure 4 shows the value of $\Delta\rho/\rho$ at this saturation, $(\Delta\rho/\rho)_{\text{satur.}}$ as a function of carrier concentration.

It should be noted that the coincidence of the curves for different temperatures over the wide range of the magnetic field was obtained by using the value of θ estimated from data obtained at low fields.

§ 3. Magnetic Behaviors

Experiments of the magnetic susceptibility have also been carried out in semiconductors in the state of the metallic impurity conduction.[6] The static susceptibility of these samples has always showed a paramagnetic deviation from the degenerate gas value. These deviations seem to be classified into two types. One of these can be explained by taking into account the deviation of the conduction band from parabolic form. The other type of deviation, observed in *n*-type silicon and *n*-type germanium, is such that the susceptibility can be represented as a sum of the degenerate gas value and a positive constant independent of the carrier concentration and temperature.

Paramagnetic susceptibility obtained from electron spin resonance experiment in phosphorus doped silicon crystals showed a marked temperature dependence and a quite different concentration dependence from that of the degenerate gas value.[10] The line width of the resonance also shows a temperature dependence which cannot be explained by the degenerate gas picture.[11] These features suggest that the observed resonance is not due to the conduction electrons, but probably due to the localized magnetic moments.

If the susceptibility obtained from resonance experiment represents the contribution from the localized magnetic moments, the temperature independence of the static susceptibility suggests an intricated nature of the distribution of the magnetization between the conduction and localized electrons. Nuclear magnetic resonance study in silicon[16] seems also suggestive for this problem.

§ 4. Temperature Dependence of the Resistivity

As mentioned in § 1. a conspicuous variation of resistivity with temperature is seen in these samples. Figure 5 is an example of this. The resistivity increases monotonically with rising temperature over the temperature region of impurity conduction. The curve shows a step at about 6°K. This step is seen only in compensated samples. Various trials[12] have been done for the explanation of the magnitude of the resistivity in these samples, including its temperature dependence. It has been pointed out that a picture of ionized impurity scattering for conduction electrons in the conduction band can explain only a part of the resistivity.[13] An approach from the random lattice, on the other hand, predicts a little higher values of resistivity.[14] One of the plausible sources of the resitivity is the electron-electron intervalley scattering. This gives a reasonable account of the temperature dependence of the resistivity above 4.2°K in samples with carrier concentration higher than $1.4\times10^{18}\text{cm}^{-3}$.

The temperature dependence below about 2°K is rather curious. The dependence is logarithmic with temperature. A logarithmic temperature

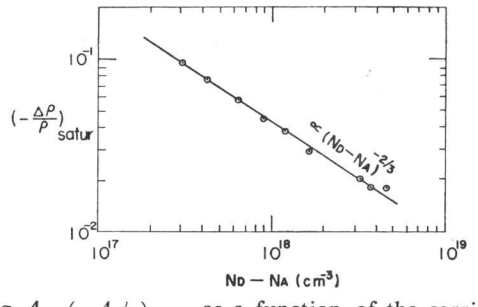

Fig. 4. $(-\Delta\rho/\rho)_{\text{satur.}}$ as a function of the carrier concentration.

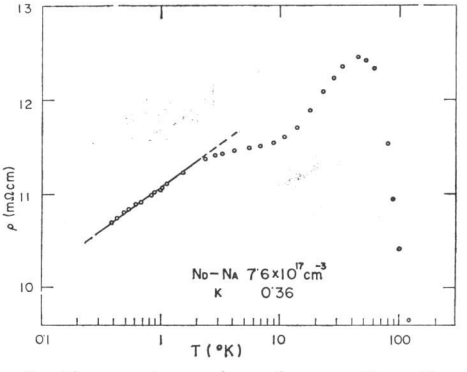

Fig. 5. Temperature dependence of antimony doped germanium. The Hall coefficient maximum is at 120°K for this sample.

dependence of resistivity exists in Cu-Mn alloys due to the s-d interaction.[15] In our case an s-d scattering mechanism has been considered for the explanation of the negative magnetoresistance effect. It may be thought that the logarithmic temperature dependence can also be explained by this scattering. However, this is not the case, because this logarithmic dependence is a reasonable explanation only when the system of the localized magnetic moments is paramagnetic. The magnetoresistance plot in Fig. 2 indicates that the magnetic system is not paramagnetic below 1°K, where the logarithmic temperature dependence holds best. The observed logarithmic variation shown in Fig. 5 must be originated from quite other mechanism than the s-d scattering.

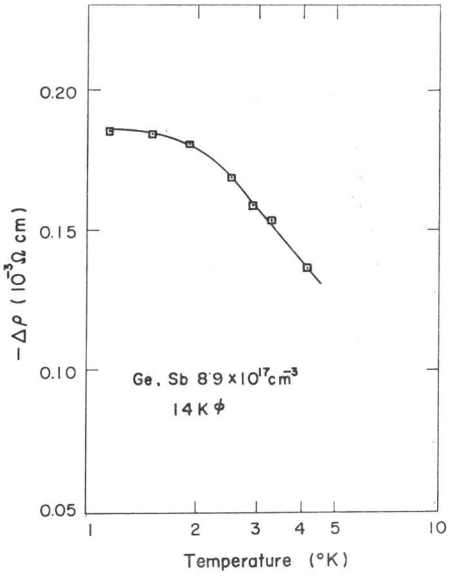

Fig. 6. The decrease of the resistivity $-\Delta\rho$ at the magnetic field of 14 kϕ vs. temperature. The sample is n-type germanium containing 8.9×10^{17}cm^{-3} antimony atoms.

It is easy to see if the logarithmic term from the s-d scattering does exist in our case. We can separate it as follows. The resistivity due to s-d scattering becomes smaller with increasing magnetic field, thus the difference between the resistivity at zero field and that at a strong field where the negative component of the magnetoresistance saturates corresponds to the magnetic scattering due to the s-d interaction. Figure 6 shows an example of the decrease of resistivity $(-\Delta\rho)_{\text{strong field}}$ versus $\log T$ plot. $(-\Delta\rho)_{\text{strong field}}$ increases as $\log T$ with decreasing temperature to below 2°K, and below this temperature $(-\Delta\rho)_{\text{strong field}}$ stays nearly constant. This behavior is consistent with the s-d picture, that is, the Curie Weiss law ceases to hold between 2°K and 1°K and below this temperature the logarithmic variation should not hold. If the logarithmic variation is represented by

$$(\Delta\rho)_{\text{strong field}}=a+b\log T\,,$$

the ratio b/a gives a measure of the magnitude of the s-d exchange energy J. For the sample shown in Fig. 6 the value of J is nearly equal to -1.8 meV. J varies as the cubic root of the carrier concentration over the range of 2×10^{17}cm^{-3} to 4×10^{18}cm^{-3}. From the magnitudes of a and J, together with an assumption that the deviation of the static susceptibility value from the calcu-

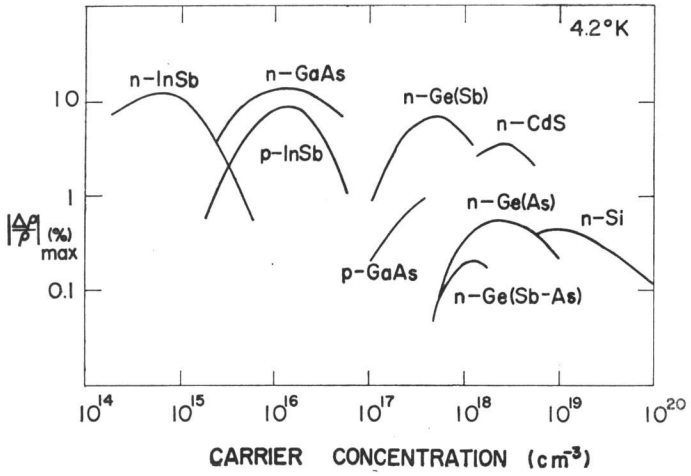

Fig. 7. $|\Delta\rho/\rho|_{\max}$, defined in Fig. 1, at 4.2°K vs. carrier concentration for various semiconductors.

lation based on the degenerate gas picture is due to the localized moments, the effective g value of the localized moments is estimated to be about 5. This is consistent with the $H/(T-\theta)$ values of 4 kϕ/°K where the negative component of the magnetoresistance saturates.

§ 5. Negative Magnetoresistance in Other Semiconductors

The negative magnetoresistance effect in semiconductors has been observed in various semiconductors, since the first report by Fritzsche and Lark-Horovitz on p-type InSb.[3] Figure 7 shows $|\Delta\rho/\rho|_{\max}$, defined in Fig. 1, at 4.2°K as a function of the carrier concentration for various semiconductors. In addition to these, it has been known that n-Te and pyrolitic and natural graphite show this effect, while p-Ge, which shows a positive anomalous effect in zero stress, becomes to show a negative magnetoresistance when a high uniaxial stress is applied.

A correlation is seen, in Fig. 7, between the concentration region where the negative effect is observed and the magnitude of $|\Delta\rho/\rho|_{\max}$ values. The curves seem to be located from left to right with the increasing magnitude of the energy gap. p-type sample shows less effect compared to the n-type samples. Though the compensation affects scarcely the magnitude of this effect, the specy of the majority impurity has a drastic influence on the magnitude. It is seen from Fig. 7 that the donor with lower activation energy results larger effect.

The shape of the curves resemble each other, suggesting that these curves can be represented by a common function with normalized ordinate and abscissa. The decrease of these curves in the higher concentration region must be related to the decrease of the statistical fluctuations. The normalization factor for the ordinate depends on the magnitude of J and the concentration of the localized magnetic moments. The factors which affect these quantities are supposed to be sensitive to the shape of the impurity potential as well as the properties of the host crystal and the concentration of the impurity.

It should be noted that the negative magnetoresistance effect is not restricted to the metallic impurity conduction. The data for GaAs in Fig. 7 was taken from the data on samples in which the resistivity varies exponentially with temperature, that is, the intermediate samples. In these samples the magnetic field makes the activation energy larger and the pre-exponential factor smaller. In the case of GaAs the decrease of resistivity due to the latter overcomes the increase due to the former, while in the case of n-Ge[15] the increase of resistivity due to the former overcomes the latter and a positive magnetoresistance is observed. If the decrease of the preexponential factor in magnetic field in the intermediate impurity conduction is also explained by the s-d picture, the existence of the localized magnetic moments are also assumed in these regions.

§ 6. Concluding Remarks

Through the tentatives described above, the idea that the role of the randomness of the impurity lattice in semiconductors is fairly well represented by the localized magnetic moments has been proved useful. Magnetic observations so far carried out seem to suggest an interesting problem concerning the nature of the localized magnetic moments. The temperature dependence of the resistivity in zero magnetic field cannot find its origin at present.

The author appreciated valuable discussions with J. Kondo, C. Yamanouchi and S. Maekawa.

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DISCUSSION

Sladek, R. J.: All the negative magnetoresistance shown in one of your slides is not associated with metallic conduction. For example, *n*-GaAs of low concentration exhibits a large maximum in the Hall coefficient at low temperatures and hence hopping type impurity conduction still exhibits also negative magnetoresistance. How do you think about this? Have you measured the magneto-resistance at lower fields than shown in your slide to verify directly the quadratic dependence of the negative magnetoresistance on magnetic field strength?

Sasaki, W.: The result for *n*-GaAs is on the intermediate samples. Partly the same thing occurs in case of *n*-Ge. In this case, the magnetic field makes the activation energy larger, on one hand, but the preexponential factor smaller, on the other. The former effect predominates the latter in the case of the intermediate *n*-Ge. Yes, I did directly verify the quadratic dependence.

Geist, D.: Your Fig. 2 (relation between maximum magnetoresistance and carrier concentration) gives me the impression that there is also a relation between effective mass and the concentration where the maximum occurs. Has this fact a true meaning?

Sasaki, W.: Yes, I think so, but the fine structures cannot be neglected. For example, the species of impurity have a drastic effect, as is seen in the case of *n*-Ge samples, doped with Sb and As.

Reiss, H.: Did Toyozawa treat the statistical problem of the random ferromagnet or merely use on internal field approximation?

Sasaki, W.: I am not sure about it.