# Resistance Anomaly and Negative Magnetoresistance in *n*-Type InSb at Very Low Temperatures

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The electrical resistivity and the magnetoresistance in *n*-type InSb containing more than  $1.8 \times 10^{14}$  cm<sup>-3</sup> carriers have been measured from 4.2 to  $0.1^{\circ}$ K. The resistivity increases logarithmically as the temperature is lowered and the relation  $\rho = a - b \log_{10}(T+T_0)$  is obtained experimentally, where *a*, *b*, and  $T_0$  are parameters which depend on the carrier concentration. The magnetoresistance at low magnetic field is negative and does not depend on the direction of the magnetic field. The temperature dependence of the magnetoresistance also includes a parameter  $T_0'$  which is nearly equal to  $T_0$  in each sample. Interpretations of the experimental results are made on the basis of the localized spin model. As a result, it is concluded that the conduction-electron scattering by the localized spin through an *s*-*d* exchange interaction may be dominant at very low temperatures in *n*-type InSb with low carrier concentration, and that an antiferromagnetic interaction between localized spins may exist. A *g* factor of the localized spin which is expected to be a few times larger than that of the isolated donor electron suggests that the localized spins arise from the same origin as discussed by Toyozawa.

#### I. INTRODUCTION

N anomalous electrical resistivity and a negative A magnetoresistance have been reported in noble metals containing traces of transition elements<sup>1</sup> and in heavily doped germanium.<sup>2</sup> For example, copper with a small amount of manganese impurities shows a minimum in its resistivity-temperature curve at about 20°K, and at lower temperatures its resistivity increases as the temperature decreases. This long-puzzling phenomenon has recently been interpreted by Kondo<sup>3</sup> as arising from the scattering of the conduction electrons by the localized impurity electrons involving the s-d exchange interaction, in which higher order terms of perturbation were taken into account. The negative magnetoresistance in dilute magnetic alloys which accompanies the resistance anomaly has also been interpreted by Yosida<sup>4</sup> as a result of the s-d exchange interaction mentioned above. Furthermore, he found theoretically a relation between the magnetization of magnetic impurities and the negative magnetoresistance in magnetic dilute alloys.

In germanium the temperature dependence of the resistivity at low temperatures is very complicated, and crystals appropriately doped with impurities show negative magnetoresistance.<sup>2</sup> Although the conduction in heavily doped germanium at low temperatures takes place in an impurity band,<sup>5</sup> the phenomenon resembles

that in the dilute magnetic alloys. Toyozawa<sup>6</sup> showed theoretically the possibility of the existence of localized spins in the metallic impurity band and tried to explain the negative magnetoresistance by introducing a scattering process like the *s*-*d* exchange interactions. Recently Sasaki<sup>7</sup> has investigated experimentally the conduction phenomena in heavily doped *n*-type Ge and has discussed his results on the basis of the localizedspin model.

In *n*-type InSb the existence of the localized spins has also been discussed by Khosla and Sladek,<sup>8</sup> and by the authors.<sup>9</sup> Khosla and Sladek have found an anomalous thermoelectric power of *n*-type InSb at low temperatures and have analyzed their results with Kasuya's theory<sup>10</sup> on the assumption of the existence of the localized spins. In our previous paper<sup>9</sup> the remarkable resistance anomaly with a logarithmic temperature dependence, and the negative magnetoresistance in *n*-type InSb at very low temperatures (0.1 to  $4.2^{\circ}$ K) were reported, and they were interpreted on the basis of the *s*-*d* interactions between the conduction electrons and the paramagnetic localized spins. It was also suggested that an antiferromagnetic interaction among the localized spins via the conduction electrons exists.

In the present paper we will report the experimental results and their interpretation in more detail. After a brief description of the experimental procedures in Sec. II, the anomalous electrical resistivity, the negative magnetoresistance, and their carrier-concentration dependences are described in Sec. III. In Sec. IV, interpretations of the experimental results are made; the logarithmic temperature dependence of the electrical resistivity and the negative magnetoresistance are

153 873

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<sup>&</sup>lt;sup>1</sup> The resistance minimum and the negative magnetoresistance in dilute magnetic alloys are summarized in D. K. McDonald, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 14, p. 137. <sup>2</sup> H. Fritzsche and K. Lark-Horovitz, Phys. Rev. 99, 400 (1955);

<sup>&</sup>lt;sup>2</sup> H. Fritzsche and K. Lark-Horovitz, Phys. Rev. **99**, 400 (1955); W. Sasaki and Y. Kanai, J. Phys. Soc. Japan **11**, 894 (1956); W. Sasaki and R. de Bruyn Ouboter, Physica **27**, 877 (1961); Y. Furukawa, J. Phys. Soc. Japan **17**, 630 (1962).

<sup>&</sup>lt;sup>8</sup> J. Kondo, Progr. Theoret. Phys. (Kyoto) 32, 37 (1964); 34, 204 (1965).

<sup>&</sup>lt;sup>4</sup> K. Yosida, Phys. Rev. 107, 396 (1957).

<sup>&</sup>lt;sup>5</sup> C. S. Hund, Phys. Rev. 79, 727 (1950).

<sup>&</sup>lt;sup>6</sup> Y. Toyozawa, J. Phys. Soc. Japan 17, 986 (1962).

<sup>&</sup>lt;sup>7</sup> W. Sasaki, J. Phys. Soc. Japan 20, 825 (1965).

<sup>&</sup>lt;sup>8</sup> K. P. Khosla and R. J. Sladek, Phys. Rev. Letters 15, 521 (1965).

<sup>&</sup>lt;sup>9</sup>Y. Katayama and S. Tanaka, Phys. Rev. Letters 16, 129 (1966).

<sup>&</sup>lt;sup>10</sup> T. Kasuya, Progr. Theoret. Phys. (Kyoto) 22, 227 (1959).

Sample No.	Carrier concentration (cm <sup>-3</sup> )	Hall mobility (10 <sup>5</sup> cm <sup>2</sup> /V sec at 4.2°K)	Fermi energy $\epsilon_F$ (meV)	$a$ ( $\Omega$ cm)	b (Ω cm)	(°К)	Т <sub>0</sub> ' (°К)
1	1.8×10 <sup>14</sup>	1.0	0.9	3.47	2.53	0.08	0.1
2	$6.0 \times 10^{14}$	1.1	2.0	0.75	0.23	0.3	0.3
3	6.5×1014	1.0	2.1	0.38	0.25	0.5	0.4
4	$1.6 \times 10^{15}$	0.93	3.8	$9.6 \times 10^{-2}$	$4.5 \times 10^{-2}$	1.0	a
5	$2.8 \times 10^{15}$	0.80	5.7	$3.2 \times 10^{-2}$	$3.5 \times 10^{-3}$	3.8	a
6	$5.0 \times 10^{15}$	0.85	8.5	$1.3 \times 10^{-2}$	$1.8 \times 10^{-3}$	10	10
7	$2.0 \times 10^{16}$	0.40	21	9.1×10 <sup>-3</sup>	$5.0 \times 10^{-4}$	6	8
8	3.3×1017	0.37	135	$4.8 \times 10^{-5}$	•••		•••

TABLE I. The list of *n*-type InSb samples which were measured in the present experiment, and parameters  $a, b, T_0, T_0'$ .

<sup>a</sup> The magnetoresistance was not symmetric when the direction of the magnetic field was reversed.

interpreted on the basis of the localized-spin model. Comparisons with the experimental results are made in Sec. V, and fairly good agreements are obtained. In this section, the interaction mechanism between the localized spins is discussed. The origin and the nature of the localized spins are also discussed, following Toyozawa's theory.

#### **II. EXPERIMENTAL PROCEDURES**

The samples measured in the present experiments were single crystals of *n*-type InSb with carrier concentrations in the range of  $1.8 \times 10^{14}$ - $3.3 \times 10^{17}$  cm<sup>-3</sup>, which are listed in Table I. They were cut in the form of prisms with dimensions of about  $3 \times 1 \times 10$  mm<sup>3</sup>, and sample surfaces were polished chemically with CP-4A solution after being ground by carborundum. Spots for electrodes were rhodium plated, and thin copper wires were soldered to the plated spots with indium. All electrodes were checked to be Ohmic at liquid-helium temperature. According to Table I, the Fermi temperatures of all the samples are higher than



FIG. 1. Resistivity of *n*-type InSb as a function of the temperature T. The resistivity is normalized to the resistivity at 4.2°K in each sample. 10°K, and this indicates that carriers are degenerate below liquid-helium temperature.

Temperatures between 4.2 and  $1.3^{\circ}$ K were obtained by controlling the vapor pressure of liquid helium, and the lowest temperature (0.1°K) was attained through adiabatic demagnetization of chrome alum. The temperatures below  $1.3^{\circ}$ K were determined from the temperature dependence of the paramagnetic susceptibility of chrome alum, which was measured by a Hartshorn bridge.

#### III. EXPERIMENTAL RESULTS

The measurements of Hall effect, electrical resistivity, and magnetoresistance were made with electric fields weaker than 1 mV/cm, where carriers do not become hot.

The Hall effect was measured in magnetic fields weaker than 70 Oe by using a Helmholtz coil, and the Hall coefficient is independent of the magnetic field below 70 Oe. Carrier concentrations of the samples are listed in Table I. The Hall coefficients in the low magnetic field are independent of temperature between 1.3 and  $4.2^{\circ}$ K.

#### A. Electrical-Resistivity Measurements

The electrical resistivity of the samples increases gradually as the temperature is lowered, and rapidly below 1°K for the samples with small carrier concentrations, as is seen in Fig. 1. The temperature dependence of the resistivity becomes weaker as the carrier concentration increases. For the sample numbered 8, no temperature dependence of the resistivity was observed down to 0.1°K. To clarify these features, the resistivity of each sample normalized by the resistivity at 4.2°K is shown in Fig. 1.

The resistivity is seen to increase logarithmically as the temperature is lowered and to approach a saturation at very low temperatures, as is shown in Fig. 2. As the carrier concentration increases, the saturating temperature shifts to the higher side. Empirically, the following expression for the temperature dependence of the resistivity was obtained:

$$\rho = a - b \log_{10}(T + T_0), \qquad (1)$$



where a, b, and  $T_0$  are positive parameters which depend on the carrier concentration  $n.^9$  The above expression fits the data on all the samples very well. In Fig. 3, the parameters a, b, and  $T_0$  are plotted against the carrier concentration. In the samples with low carrier concentrations, the carrier-concentration dependences of these parameters are approximately

$$a \propto n^{-2},$$
  

$$b \propto n^{-2.5},$$
  

$$T_0 \propto n^{1.5}.$$
(2)

It is noticeable that the parameter  $T_0$ , which characterizes the saturation at very low temperatures, increases with the carrier concentration.

#### **B.** Magnetoresistance

The transverse and longitudinal magnetoresistance effects of the samples were measured with magnetic fields weaker than 70 Oe between 0.1 and 4.2°K. In these measurements, the temperature of the demagnetized paramagnetic salt did not increase appreciably on the application of the weak magnetic field, and so the temperature of the sample was believed to be kept unchanged during each run of the magnetoresistance measurement. Magnetoresistance measurements for

stronger magnetic fields (up to 3 kOe) were also made between 1.3 and 4.2°K.

For each measurement of the resistivity in the presence of the magnetic field, four readings were taken with opposite directions of sample current and opposite directions of magnetic field to eliminate thermal electromotive forces and to see whether the magnetoresistive ratio is an even function of the magnetic-field strength. In some samples, the magnetoresistances were not symmetric when the direction of the magnetic field was reversed, and they were rejected from the magnetoresistance data in the present paper.

A typical example of the magnetoresistance is shown in Fig. 4. The transverse magnetoresistance is negative in the weak magnetic fields, reaches its minimum at about 500 Oe, and then gradually turns positive as the magnetic field increases.

In Fig. 5 the angular dependences of the magnetoresistance at various magnetic fields are shown. The angular dependences of the magnetoresistance were not observed in magnetic fields (weaker than 70 Oe), and weak angular dependences were observed in the magnetic fields stronger than 500 Oe. It was also found that the transverse magnetoresistance in the weak magnetic field does not depend on the direction of the magnetic field lying in the plane perpendicular to the sample current.

In a magnetic field weaker than 50 Oe, the magneto-



n.





FIG. 5. Magnetoresistance of *n*-type InSb at 1.3 and  $4.2^{\circ}$ K. The magnetic field is rotated in the plane containing the sample current and a line perpendicular to the sample plane. (Sample No. 1.)

resistance is negative and can be expressed in the form<sup>9</sup>

$$-\Delta\rho/\rho = -[\rho(H) - \rho(0)]/\rho(0) = S(T)H^2, \quad (3)$$

as is shown in Fig. 6. The magnetoresistance coefficient S(T) depends on the temperature T and the carrier concentration n. The coefficient S(T) increases as the temperature is lowered. According to the localizedspin model which will be discussed in the next section, S(T) is proportional to the square of the susceptibility of the localized spins. Thus, S(T) is plotted against temperature in Fig. 7, and it was found that

$$\{S(T)\}^{-1/2} \propto (T + T_0') \tag{4}$$

above 1°K, and S(T) is almost constant below about 1°K. In the above expression,  $T_0'$  is a positive parameter with the dimension of temperature, and increases with the carrier concentration.

The parameter  $T_0'$  was actually determined more easily as follows.  $(-\Delta \rho / \rho)^{-1/2}$  is plotted against temperature at a constant magnetic field, and  $T_0'$  is obtained by extrapolating the experimental points, as is shown in Fig. 8. It is interesting that the parameter  $T_0'$  is nearly equal to the parameter  $T_0$  appearing in the expression (1) in each sample. The values for  $T_0'$ and  $T_0$  in these experiments are given in Table I.

### **IV. INTERPRETATIONS**

The carrier concentrations of all the samples in the present experiments are independent of temperature below 4.2°K, as is seen from the results of the Hall measurements. The observed resistance anomaly and the negative magnetoresistance, therefore, must arise from an electron-scattering process which appears in *n*-type InSb at very low temperatures.

At first we will discuss briefly some aspects of the electron conduction in InSb. The effective mass  $m^*$  of the electrons in the conduction band is only 0.013 times the rest mass  $m_0$  of a free electron.<sup>11</sup> Accordingly,

the Fermi temperature  $T_F$  of the conduction electrons is very high in comparison with the temperatures at which the present experiments were performed (Table I). The carriers, then, are highly degenerate even in the sample with the smallest carrier concentration.

Moreover, the effective Bohr radius  $a_B^*$  of the conduction electron is as large as 640 Å, so that the parameter  $r_s = r_{av}/a_B^*$  is only 1.7, even in the sample with the smallest carrier concentration  $(r_{\rm av}$  is the average distance between electrons). Comparing this value with those usual in metals  $(r_s=3-7)$ , we can say that the carrier concentration in *n*-type InSb is very high.



The donor level calculated by the effective-mass approximation lies only 0.7 meV below the bottom of the conduction band. Furthermore, the activation process of electrons from the donor levels in n-type InSb is not observed in the samples with carrier concentration higher than 1014 cm-3, and the impurity conduction occurs only in the ultrapure samples with the carrier concentration of the order of 1013 cm-3.12 Therefore, it is probable that the impurity band does not exist independently of the conduction band in our samples, and that the conduction takes place in the conduction band. This conjecture is supported by the fact that the mobility of the carriers in the sample used in the present experiments is large even at low temperatures (see Table I).<sup>13</sup>

Kondo showed<sup>3</sup> that the logarithmic temperature dependence of the electrical resistivity in dilute magnetic alloys at low temperatures comes from the scat-

<sup>&</sup>lt;sup>11</sup> G. Dresselhaus, A. F. Kip, C. Kittel, and C. Wagoner, Phys. Rev. 98, 556 (1955).

 <sup>&</sup>lt;sup>12</sup> D. N. Nasledov, J. Chem. Phys. 57, 479 (1960).
 <sup>13</sup> It may be said that this statement is also supported by the following two theoretical investigations: P. A. Wolff [Phys. Rev. 126, 405 (1962)] has treated the band structure of very degenerate semiconductors by using many-body perturbation theory and has obtained the result that the influence of impurity potential is small for electrons near the Fermi surface and becomes important near the bottom of the band. According to F. Stern and R. M. Talley's calculation [Phys. Rev. 100, 1638 (1955)], the impurity level has a finite width which is comparable with the depth of the isolated donor level in n-type InSb with carrier concentration  $n = 2 \times 10^{14} \text{ cm}^{-3}$ 

tering of the conduction electrons by localized paramagnetic spins through s-d exchange interactions. The resemblance between the temperature dependences of the resistivity in n-type InSb and those in dilute magnetic alloys suggests that a similar electron-scattering mechanism contributes to the resistivity in n-type InSb also. This is consistent with the observed negative magnetoresistance in n-type InSb reported here.

Besides the scattering of the electrons due to the s-d interactions, the scattering of the electrons by ionized donor potentials contributes to the electrical resistivity in n-type InSb, though it has no temperature dependence.

We assume, then, that the observed electrical resistivity in n-type InSb is determined by two electronscattering mechanisms: (a) the ionized-impurity scattering, and (b) the scattering by the localized spins due to the *s*-*d* interactions. As the wavelength of the conduction electron is not very short in comparison with the average distance between donors, it might be possible that multiple scattering or the scattering due to the combination of the above two mechanisms affects the resistivity to some extent. To simplify the problem, however, we will neglect these effects in the following calculations.



A. Ionized-Impurity Scattering

The conduction-electron scattering by ionized donors in InSb at 80°K was fully discussed by Bate *et al.*<sup>14</sup> They made use of Kane's model<sup>15</sup> for the conduction band of InSb, and obtained a formula slightly different from the Brooks-Herring formula. They had further improved the formula by taking into account a correction of the screening based on Takimoto's treatment.<sup>16</sup>

In order to estimate the electron mobility due to ionized-impurity scattering at 4.2°K, we used Bate et al.'s numerical results in the carrier-concentration range higher than  $10^{16}$  cm<sup>-3</sup>, because in this range the carriers are degenerate even at  $80^{\circ}$ K. On the other hand, the carriers are degenerate below  $4.2^{\circ}$ K, but are not degenerate at  $80^{\circ}$ K in the carrier-concentration range lower than  $10^{16}$  cm<sup>-3</sup>, and so Bate *et al.*'s results cannot be used at  $4.2^{\circ}$ K. We therefore calculated the electron mobility at  $4.2^{\circ}$ K by the Brooks-Herring formula and joined it smoothly to Bate *et al.*'s results in the high concentration range. The electrical resistivity determined from the ionized-impurity scattering,  $\rho_I$ , is independent of temperature in the temperature range where the carriers are degenerate, as in the present experiments.

#### B. Scattering by Localized Spins

As was discussed by Kondo,<sup>3</sup> the probability for scattering of the conduction electron by the localized spins depends strongly on the energy of the conduction electron, because of the dynamical character of the localized-spin system. In his calculation of the resistivity of dilute magnetic alloys, he dealt with the perturbing Hamiltonian of the *s*-*d* interaction given by Kasuya<sup>17</sup> to the second Born approximation, and found a logarithmic temperature dependence of the resistivity.

The interaction Hamiltonian given by Kasuya, however, cannot be applied in its original form to the localized-spin system in *n*-type InSb, because the character of the localized spin in *n*-type InSb is different from that of the localized spin in dilute magnetic alloys. In dilute magnetic alloys, the localized spin is well localized in a unit cell with the volume  $\Omega$ , while the localized spin in *n*-type InSb is considered to spread over a wide region of volume  $\Omega'$ , containing many unit cells. The perturbing Hamiltonian for the *s*-*d* interaction in *n*-type InSb is, then, given by

$$H' = -\frac{J'}{N'} \sum_{\mathbf{n},\mathbf{k},\mathbf{k}'} e^{i(\mathbf{k}-\mathbf{k}')\mathbf{R}_{\mathbf{n}}} \{ (a^{*}_{\mathbf{k}+}a_{\mathbf{k}'+} - a^{*}_{\mathbf{k}-}a_{\mathbf{k}'-}) \mathbf{S}^{z_{\mathbf{n}}} + a^{*}_{\mathbf{k}+}a_{\mathbf{k}'-}\mathbf{S}^{-}_{\mathbf{n}} + a^{*}_{\mathbf{k}-}a_{\mathbf{k}'+}\mathbf{S}^{+}_{\mathbf{n}} \}, \quad (5)$$



<sup>17</sup> T. Kasuya, Progr. Theoret. Phys. (Kyoto) 16, 45 (1956).

<sup>&</sup>lt;sup>14</sup> R. T. Bate, R. D. Baxter, F. J. Reid, and A. C. Beer, J. Phys. Chem. Solids **26**, 1205 (1965).

<sup>&</sup>lt;sup>15</sup> E. O. Kane, J. Phys. Chem. Solids 1, 249 (1956).

<sup>&</sup>lt;sup>16</sup> N. Takimoto, J. Phys. Soc. Japan 14, 1142 (1959).

where  $\mathbf{R}_n$  denotes the position vector of the **n**th localized spin, whose spin operator is denoted by  $\mathbf{S}_n$ , and  $a_{\mathbf{k}\pm}$ and  $a^*_{\mathbf{k}\pm}$  are the annihilation and creation operators of the conduction electron with the wave vector **k** and + or - spin. N' is defined by  $N'\Omega' = N\Omega$ , where N is the total number of unit cells in the crystal. J' is the exchange integral between a conduction electron and a localized spin, and may be written

$$J' = N'e^{-i(\mathbf{k}-\mathbf{k}')\mathbf{R}_{n}} \times \int \frac{\varphi_{\mathbf{k}}^{*}(\mathbf{r}_{1})\varphi_{dn}^{*}(\mathbf{r}_{2})e^{2}\varphi_{\mathbf{k}'}(\mathbf{r}_{2})\varphi_{dn}(\mathbf{r}_{1})}{r_{12}} d\mathbf{r}_{1}d\mathbf{r}_{2}, \quad (6)$$

where  $\varphi_k$  is the Bloch function of the conduction electron normalized in the entire crystal, and  $\varphi_{dn}$  is the wave function of the *n*th localized spin spread over the volume  $\Omega'$ .

The calculation of the electrical resistivity of n-type InSb due to the *s*-*d* interactions was performed by using the perturbing Hamiltonian [Eq. (5)] in a similar way to that in Kondo's theory; the result is

$$\rho_{\rm spin} = c \rho_M \{ 1 + 4n(\epsilon_F) (N/N') J' \ln(kT/\epsilon_F) \}, \quad (7)$$

and

$$\rho_{M} = \frac{N}{N'} \frac{3\pi m^{*} J'^{2} S(S+1)}{2e^{2} \epsilon_{F} \hbar} \frac{V}{N'}, \qquad (8)$$

where S is the magnitude of the localized spin,  $n(\epsilon_F)$  is the density of state at Fermi energy, and c is the fraction of localized spins per unit cell. In Eq. (7), the first term comes from the first-order Born approximation, and the second term from the second-order approximation.

Summarizing the above discussions, we can write the electrical resistivity of n-type InSb at low temperatures as follows:

$$\rho = \rho_{\rm spin} + \rho_I$$
$$= c\rho_M \left\{ 1 + 4n(\epsilon_F) \frac{N}{N'} J' \ln(kT/\epsilon_F) \right\} + \rho_I. \tag{9}$$

#### C. Negative Magnetoresistance

The negative magnetoresistance observed in *n*-type InSb cannot be explained by the usual mechanisms of magnetoresistance. As was pointed out by Yosida,<sup>4</sup> however, there is a possibility of interpreting the negative magnetoresistance by introducing the *s*-*d* interactions discussed in Subsection B. According to Yosida's theory, the magnetoresistance in low magnetic fields is expressed by

$$-\Delta\rho/\rho = \alpha M^2, \qquad (10)$$

where M is the average magnetization of the localized spins, and  $\alpha$  is a constant. The magnetoresistance coefficient S(T) in the preceding section, then, is repre-

TABLE II. The exchange integral J' and the concentration of localized spins estimated from the experimental results.

Sample No.	Carrier concentration (cm <sup>-3</sup> )	(J'/N') (eV cm <sup>3</sup> )	Concentration of localized spins cN (cm <sup>-3</sup> )
1 2 3 4 5 6 7	$\begin{array}{c} 1.8 \times 10^{14} \\ 6.0 \times 10^{14} \\ 6.5 \times 10^{14} \\ 1.5 \times 10^{15} \\ 2.8 \times 10^{15} \\ 5.0 \times 10^{15} \\ 2.0 \times 10^{16} \end{array}$	$\begin{array}{r} -4.7 \times 10^{-18} \\ -1.9 \times 10^{-18} \\ -2.2 \times 10^{-18} \\ -1.2 \times 10^{-19} \\ -3.0 \times 10^{-19} \\ -5.5 \times 10^{-20} \\ -1.0 \times 10^{-20} \end{array}$	$\begin{array}{c} 4.6 \times 10^{13} \\ 1.3 \times 10^{14} \\ 0.9 \times 10^{14} \\ 1.3 \times 10^{14} \\ 8.0 \times 10^{14} \\ a \\ a \end{array}$

\* The derived concentration of localized spins exceeds the carrier concentration of the sample. This seems to come from neglecting  $\rho_I$  in the above estimation, which is a major part of the resistivity for samples with large carrier concentration.

sented in terms of  $\alpha$  as follows:

$$S(T) = \alpha X^2, \tag{11}$$

where  $\chi$  is the susceptibility of the localized spin system. Therefore, if the spin system is completely paramagnetic,  $(-\Delta \rho / \rho)^{1/2}$  should be given by a function of H/T.

## V. COMPARISON WITH THE EXPERIMENTAL RESULTS

The observed temperature dependence of the electrical resistivity and the negative magnetoresistance of n-type InSb at very low temperatures in the present experiments will be discussed along with the interpretation described in the preceding section.

## A. Temperature Dependence of the Electrical Resistivity

The observed logarithmic temperature dependence of the electrical resistivity is well explained in the temperature range  $T \gg T_0$  by the *s*-*d* exchange interaction if the existence of the localized spins in *n*-type InSb is assumed.

As was discussed in the preceding section, the electrical resistivity  $\rho$  consists of  $\rho_I$ , due to the ionizedimpurity scattering, which is independent of temperature, and  $\rho_{\rm spin}$ , which gives the logarithmic temperature dependence. In the temperature range  $T \gg T_0$ , the observed resistivity is given by the expression (1) as

$$\rho = a - b \log_{10} T. \tag{12}$$

In order to investigate the resistivity due to the *s*-*d* interaction, we must subtract the resistivity  $\rho_I$  from Eq. (12). Transforming Eq. (12) into

$$\rho = a - b \log_{10}(\epsilon_F/k) - b \log_{10}(kT/\epsilon_F)$$
  
=  $a' - b' \ln(kT/\epsilon_F)$ , (13)

we can say that  $a'=a-b \log_{10}(\epsilon_F/k)$  consists of  $\rho_I$  and the first term of Eq. (7) which comes from the first order *s*-*d* interactions. *a* and *a'* are plotted in Fig. 9. In this figure, *a'* has somewhat more scatter in the high carrier-concentration range, and this comes from ambiguity in the determination of the parameter b in the experiments, as the temperature dependence of the resistivity is weak in the high carrier-concentration range. In order to estimate the numerical values of the exchange integral J' and the concentration c of the localized spins by the comparison of Eq. (13) with Eq. (7), the exact values of  $\rho_I$  in each sample must be used. An exact numerical estimate of  $\rho_I$  in each sample, however, cannot be made, since there remain unknown factors such as the effect of compensation, the effect of screening of the impurity potential at low temperatures, the multiple scattering, and so on. Since in the sample with the lowest carrier concentration the resistivity has the strongest temperature dependence, it is expected that  $\rho_I$  is only a small fraction of a'. Thus  $\rho_I$  is neglected in the comparison of Eq. (9) with the empirical expression Eq. (13).

The ratio of the first and the second terms of Eq. (7),  $4n(\epsilon_F)(N/N')J'$ , corresponds to b'/a' in Eq. (13). The Fermi energy  $\epsilon_F$  in each sample is given in Table I. The density of states at the Fermi energy  $n(\epsilon_F)$  was calculated with the effective mass  $m^*=0.013m_0$ . The results obtained for J'/N' and c are shown in Table II. In this table, J'/N' decreases and c increases as the carrier concentration increases. But taking into account  $\rho_I$ , which is neglected in the above calculation, we may expect that the carrier-concentration dependence of J'/N' becomes weaker, and then the dependence of c is changed to some extent, especially in the high carrierconcentration range. With such a treatment of the temperature dependence of the electrical resistivity, only the ratio J'/N' is obtained, and not J' and N'separately. However, we estimate the magnitude of the exchange integral J' in the lowest-carrier-concentration sample, taking the effective Bohr radius as the spreading of the wave function of the localized spin. Then J' is of the order of -1 meV. In the Appendix, we discuss the possibility that the exchange integral J'is negative, a possibility which arises when we take into account the mixing of the wave function of the localized spin and that of the conduction electron.

The existence of the parameter  $T_0$  in the expression (1) for the electrical resistivity may come from the presence of the interaction among the localized spins via conduction electrons, and this will be discussed in the following subsection.

### **B.** Negative Magnetoresistance

As was mentioned in the preceding section, the magnetoresistance of n-type InSb at low temperatures is negative in weak magnetic fields, reaches its minimum at about 500 Oe, and then turns positive as the magnetic field increases.

According to Yosida's theory,<sup>4</sup> which was described in the preceding section, the negative magnetoresistance is proportional to the square of the average magneti-



zation of the localized-spin system. Thus, it is expressed as

$$-\Delta \rho / \rho = \alpha M^2 = \alpha \chi^2 H^2. \tag{14}$$

Moreover, the conduction-electron scattering by this process must be independent of the direction of the magnetic field, since the *s*-*d* interaction is isotropic and the conduction band in *n*-InSb is spherical. This leads to the negative magnetoresistance which does not depend on the angle between the magnetic field and current directions.

In the present experiments, the magnetoresistance is negative and proportional to the square of the magnetic field, as is shown in Fig. 6, and it does not depend on the angle between the magnetic field and the current, in contrast with the positive magnetoresistance in higher magnetic fields, which shows an angular dependence. Such a coincidence between the experimental results and the theory seems to indicate that the negative magnetoresistance in n-InSb comes from the s-d interactions between the conduction electrons and the localized spins.

In order to investigate the magnetic properties of the localized spin, the values of  $(-\Delta\rho/\rho)^{1/2}$  are plotted in Fig. 10 against  $H/(T+T_0')$  for a magnetic field Hweaker than 70 Oe and for temperatures between 4.2 and 0.2°K. Here  $T_0'$  is the parameter which appeared in the expression (4) in the description of the temperature dependence of the magnetoresistance coefficient S(T). It should be noted that the experimental values of  $(-\Delta\rho/\rho)^{1/2}$  are better described by a function of  $H/(T+T_0')$  than of H/T. This means that the temperature dependence of the susceptibility of the localizedspin system obeys the Curie-Weiss law, and the parameter  $T_0'$  can be taken as the paramagnetic Curie temperature of the localized-spin system.

Furthermore, it is seen from Fig. 10 that  $(-\Delta\rho/\rho)^{1/2}$ as a function of  $H/(T+T_0')$  has a form similar to that of the Brillouin function. From the curvature of this function and the saturation characteristics of the magnetoresistance at higher magnetic fields, the g factor where



FIG. 10. Plot of  $(-\Delta\rho/\rho)^{1/2}$  against  $H/(T+T_0')$ , where magnetic field H is in Oe and the temperature T is in °K. (a) Sample No. 1  $(T=1.3-4.2^{\circ}\text{K})$ . (b) Sample No. 3  $(T=0.2-4.2^{\circ}\text{K})$ .

of the localized spin in *n*-type InSb is estimated to be of the order of  $10^2$  (about 200 in the sample No. 1). Such a value of the g factor is several times larger than that of a conduction electron, g = -55, at the bottom of the conduction band.<sup>18</sup>

Toyozawa<sup>6</sup> discussed theoretically the possibility that as a result of the collective nature of the localized spin, the localized spin in semiconductors has a magnetic moment several times as large as that of an electron bound to an isolated impurity. In *n*-type InSb containing a carrier concentration of more than  $10^{14}$ cm<sup>-3</sup>, the  $r_s$  is rather small, as was noted before, and this means that the collective nature of the localized spins may be confidently assumed.

The existence of the positive parameter  $T_0'$  in the expression (4) for the negative magnetoresistance, which corresponds very nearly to the parameter  $T_0$  in the expression (1) for the temperature dependence of the electrical resistivity, suggests the presence of the antiferromagnetic coupling among the localized spins. An estimate of the magnitude of the interaction among localized spins was made as follows: First we assume that the interaction among localized spins in *n*-type InSb at very low temperatures comes from the indirect interaction via the conduction electrons. This type of interaction is calculated from the second-order effect of the s-d exchange interaction between the localized spins and the conduction electrons (Ruderman-Kitteltype interaction). Yosida's theory,<sup>19</sup> which deals with dilute magnetic alloys, is modified in the same way as in Sec. IV, and the second-order perturbation energy is given by

$$H^{\prime (2)} = (3n/N^{\prime})^2 \frac{2\pi}{\epsilon_F} J^{\prime 2} \sum_{\mathbf{n},\mathbf{m}} F(2k_F R_{\mathbf{n}\mathbf{m}}) (\mathbf{S}_{\mathbf{n}} \cdot \mathbf{S}_{\mathbf{m}}), \quad (15)$$

$$F(x) = (x \cos x - \sin x) / x^4.$$
(16)

Here,  $R_{nm}$  is the distance between the localized spins **n** and **m** (represented by the spin operators  $S_n$  and  $S_m$ , respectively) and  $k_F$  is the wave number of a conduction electron at the Fermi surface. Equation (15) gives the ferromagnetic interaction between the localized spins, while the interaction in n-type InSb is considered as antiferromagnetic, as was mentioned above. Yosida,<sup>19</sup> however, has pointed out that the spatial dependence of the exchange integral would change to antiferromagnetic the coupling between the localized spins. For the sample with the smallest carrier concentration, the estimated  $T_0'$  from Eq. (15) is about 2°K, and this is not far from the value  $T_0' = 0.1^{\circ}$ K determined from the experiments. In this estimation, the distance  $R_{nm}$ between the localized spins is replaced by the average distance between the localized spins, the concentration of which is obtained from Table II. But the carrierconcentration dependence of  $T_0$ , determined experimentally as in Eq. (2), cannot be explained reasonably from Eq. (15). This is, we think, due to the fact that the direct application of Eq. (15) to the localized-spin system in n-type InSb is not plausible. It is actually quite difficult to take into account the effect of the random distribution of the localized spins in the above estimation, even if the Ruderman-Kittel-type interaction is dominant. Moreover, the wave function of the localized spin in *n*-type InSb is spread over a large volume, and it may be very complicated, as can be expected from the mixing between the wave functions of the localized spins and conduction electrons, or from the collective nature of the localized spins. Therefore, the expression for the indirect-exchange interaction in such a case may be greatly different from Eq. (15).

Besides the indirect-exchange interaction between the localized spins, the direct-exchange interaction may

<sup>&</sup>lt;sup>18</sup> G. Bemski, Phys. Rev. Letters 4, 62 (1959).

<sup>&</sup>lt;sup>19</sup> K. Yosida, Phys. Rev. 106, 893 (1957).

contribute to the coupling among the localized spins in n-type InSb. Toyozawa<sup>6</sup> has suggested that the direct exchange may play a major role in the low carrier-concentration range in n-type Ge.

#### C. Localized Spins in *n*-Type InSb

As was discussed in the earlier part of this section, the experimental results are well explained by assuming conduction-electron scattering by the localized spins through an *s*-*d* exchange interaction. The origin and the character of the localized spins will now be discussed.

In dilute magnetic alloys, the origin of the localized spin is the magnetic impurities, the wave function of which is almost limited in the unit cell.<sup>20</sup> In the degenerate semiconductors, on the other hand, the localized spin should be related to the randomly distributed donor states, since no magnetic impurities are added in the doping. Toyozawa<sup>6</sup> discussed in detail the possibility of the existence of the localized spins in the case of the metallic impurity band of *n*-type Ge. In this case, he showed that the localized spins appear as the result of electron correlation and random array of impurity sites. If the site is isolated enough, there is the possibility that the effect of electron correlation overcomes that of electron transfer, resulting in the appearance of localized free spins. If, however, the site is too isolated from other sites, it does not act as a scatterer, since the other electrons are hardly able to move through the site, and, consequently, its spin direction does not influence the transport properties. Therefore, the appearance of the localized spin on a site depends on the impurity distribution around it.

In *n*-type InSb, on the other hand, the electronic conduction occurs in the conduction band, and so the correlation between the conduction electron and the electron bound to the impurity site is very weak. Consequently, the well-isolated neutral donor may also be able to behave as a localized spin which scatters the conduction electrons. If a well-isolated neutral donor, surrounded by a volume  $v_0$  in which no other impurity exists, is taken as the origin of the localized spin, the concentration c of the localized spins is expressed in terms of n, that is,

$$c \propto n e^{-v_0 n}. \tag{17}$$

and

The concentration c expected from Eq. (17) decreases very rapidly as n increases, while the c, estimated from the experimental results, increases. This suggests that the isolated neutral donors play a minor role as the origin of the localized spins. Since it is thought that the bottom of the conduction band has a character like the impurity band, the model for the localized spins discussed by Toyozawa may be preferable in n-type InSb. The large g factor observed in the present experiments seems to support such a conclusion.

### ACKNOWLEDGMENTS

The authors' heartfelt thanks are due to Takeshi Kamiya and Yasuhiro Shiraki for their helpful contributions to this work. The authors are sincerely grateful to Professor Yasutada Uemura and Professor Hiroshi Kamimura for fruitful discussions and suggestions, and also to Dr. Kiichi F. Komatsubara for supplying the samples. The latter part of this work was financially supported by the Central Research Laboratory of Hitachi Company, Ltd.

### APPENDIX: THE NEGATIVE VALUE OF THE EXCHANGE INTEGRAL J'

The exchange integral J' between the conduction electron and the localized spin in *n*-type InSb is expected to be negative from the observed temperature dependence of the electrical resistivity. In dilute alloys, it was shown by Kondo,<sup>21</sup> taking Gd metal as an example, that the effect of mixing wave functions of conduction electrons and localized electrons may lead to a negative exchange integral J. The sign of J is determined by the balance between the direct-exchange interaction, which is positive, and the negative contribution from the mixing effect. We discuss the problem of the negative J in *n*-type InSb along lines similar to those of Kondo's treatment.

We shall consider the two-electron problem, one electron in the localized state denoted by the orbital wave function  $\varphi_i(\mathbf{r})$  and the spin function  $\Theta(\zeta)$ , and the other in the conduction band denoted by  $\varphi_k(\mathbf{r})$  and  $\chi(\zeta)$ . The unperturbed state  $\Psi_q$  is expressed in the form

$$\Psi_{g} = (1/\sqrt{2}) \sum_{P} \delta_{P} P \varphi_{k}(\mathbf{r}_{1}) \varphi_{i}(\mathbf{r}_{2}) \chi(\zeta_{1}) \Theta(\zeta_{2}). \quad (A1)$$

First we consider a perturbation process in which a conduction electron with wave vector **k** and z component of spin  $\zeta$  is transferred to an empty level of  $\varphi_i$ , and then returns to a conduction band with wave vector **k'**. For the sake of simplicity, we consider only an *s*-like function for  $\varphi_i$ . Then the corresponding excited state and the second-order perturbation energy are

$$\Psi_e = \frac{1}{\sqrt{2}} \sum_{P} \delta_P P \varphi_i(\mathbf{r}_1) \varphi_i(\mathbf{r}_2) \Theta(\zeta_{1}, \zeta_{2})$$
(A2)

$$-\frac{\langle \Psi_{g'} | V_{sd} | \Psi_e \rangle \langle \Psi_e | V_{sd} | \Psi_g \rangle}{\epsilon_e^- - \epsilon_F}, \qquad (A3)$$

where  $\epsilon_{e} - \epsilon_{F}$  is the energy necessary to take an electron near the Fermi surface and to replace it on  $\varphi_{i}$ . The quantity  $V_{sd}$  is the perturbation which causes electron transfer.

We consider next a process in which the localized electron is excited to a level in the conduction band and then returns to the localized state  $\varphi_i$ .

<sup>&</sup>lt;sup>20</sup> P. W. Anderson, Phys. Rev. **124**, 41 (1961): P. A. Wolff, *ibid*. **124**, 1030 (1961).

<sup>&</sup>lt;sup>21</sup> J. Kondo, Progr. Theoret. Phys. (Kyoto) 28, 846 (1962).

Summing up these two processes, the total Hamilibian is the radial part of  $\varphi_i(\mathbf{r})$ ; and  $j_0$  is the zeroth-order tonian for the mixing effect is expressed as

$$H' = \frac{A_0}{N'} \sum_{\mathbf{n},\mathbf{k},\mathbf{k}'} e^{i(\mathbf{k}-\mathbf{k}')\mathbf{R}_{\mathbf{n}}} \{ (a^*_{\mathbf{k}'+}a_{\mathbf{k}+} - a^*_{\mathbf{k}'-}a_{\mathbf{k}-})S^z_{\mathbf{n}} + a^*_{\mathbf{k}'-}a_{\mathbf{k}+}S^+_{\mathbf{n}} + a^*_{\mathbf{k}'+}a_{\mathbf{k}-}S^-_{\mathbf{n}} \}, \quad (A4)$$

where

and

$$A_0 = V_0^2 \left\{ \frac{1}{\epsilon_e^- - \epsilon_F} + \frac{1}{\epsilon_e^+ - \epsilon_F} \right\}, \qquad (A5)$$

$$V_0^2 = (4\pi)^{1/2} \int_0^\infty P(\mathbf{r}) V_{sd}(\mathbf{r}) j_0(\mathbf{r}) r^2 d\mathbf{r}.$$
 (A6)

Here, it is assumed that  $V_{sd}(\mathbf{r})$  is spherical;  $P(\mathbf{r})$ 

spherical Bessel function.

The value  $A_0$  in (A4) is positive. Comparing Eq. (A4) with Eq. (5) in Sec. IV, we may conclude that the mixing of the wave functions of conduction and localized electrons gives the negative contribution  $-A_0$  to the exchange integral. Then the sign of the exchange integral J' is determined by the two competing effects, the direct-exchange integral, which is positive, and the effect of mixing, which is negative. Therefore a negative J' is possible if the effect of mixing is appreciably large. It is possible that this mixing effect for the s-d interaction in *n*-type InSb is very large, since the energy level of the localized state seems to exist not far from the Fermi level, as discussed in Sec. IV.

PHYSICAL REVIEW

VOLUME 153, NUMBER 3

15 JANUARY 1967

# **Excitons in Degenerate Semiconductors**

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The band-to-band optical absorption is calculated for a direct-band-gap semiconductor that has one band degenerate n or p type. The degenerate band is treated as a high-density Fermi gas. It is shown that exciton states, arising from the electron-hole Coulomb attraction, still affect the optical absorption. The calculations show that exciton states cause a logarithmic singularity in the absorption at the Burstein edge. This singularity is present at a moderate density of electrons or holes in the degenerate band, but it gradually disappears in the high-density limit. Lifetime broadening could make the logarithmic singularity difficult to observe at higher densities.

#### I. INTRODUCTION

**TALENCE**-band-to-conduction-band optical-absorption experiments have provided much information about insulating or lightly doped semiconduc-



FIG. 1. Optical absorption in a semiconductor with a degen-erate conduction band. The onset of optical absorption is at  $\omega = E_G + p_F^2/2\nu$ , where  $E_G$  is the energy gap,  $p_F$  is the electron Fermi momenta, and  $\nu$  is the electron-hole reduced mass.

tors. Of particular fruitfulness has been the study of exciton states, the electron-hole bound states which drastically alter the shape of the absorption edge in semiconductors where the lowest transition is direct. The present calculation is concerned with optical-absorption processes in direct-gap semiconductors which have one band sufficiently doped that it can be viewed as a degenerate electron gas at low temperatures. The case where the conduction band is doped is indicated in Fig. 1, where the transition of interest is from the heavyhole band. The results of this calculation show that exciton effects, in the form of final-state electron-hole Coulomb scattering, still drastically affect the opticalabsorption spectra. This seems to occur even in the limit that the conduction electrons can be viewed as a high-density electron gas.

Elliott<sup>1</sup> showed that optical absorption in semiconductors should be viewed as the creation of an electronhole pair. In his calculation for insulating semiconductors, the electron-hole Coulomb interaction was included by solving Schrödinger's equation for a hydrogen atom. The inclusion of these Wannier exciton states provided

882

<sup>&</sup>lt;sup>1</sup> R. J. Elliott, Phys. Rev. 108, 1384 (1957).