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THE METAL-NON METAL TRANSITION IN DOPED SEMICONDUCTORS

W. SASAKI

Department of Physics, Faculty of Science, University of Tokyo, Hongo-7, Tokyo, Japan

Résumé. — Les données du transport électrique, de la susceptibilité magnétique et de la RMN dans Si dopé au P sont examinées pour donner une image de la transition métal-non métal du semi-conducteur dopé : la percolation des grappes de donneurs qui subissent la transition locale de Mott. Les expériences au-dessous de 1K suggèrent une possibilité pour les électrons dans les échantillons métalliques de se condenser en nouvelles phases aux températures très basses.

Abstract. — Data of electric transport, magnetic susceptibility, and NMR in P-doped silicon are examined to give a picture of metal-non metal transition in doped semiconductor: the metallic transition is percolation of donor clusters which have undergone local Mott transition. Experiments below 1K suggest a possibility for electrons in metallic samples to condense into new phases at very low temperatures.

1. Introduction. — In 1956 Mott [1] proposed a mechanism for the transition to metallic state of a hypothetical crystal consisting of hydrogen atoms. This mechanism is formulated on the basis of an idea that the Coulomb field, binding each electron around the host positive ion, is screened in a cooperative way when the lattice constant of the crystal is reduced below a critical value. This mechanism was applied to the explanation of MNM transition in doped semiconductor. However, impurity atoms in doped semiconductor are distributed in a random way, and this randomness made the problem very complicated. Recently an improved mechanism, called Mott-Hubbard-Anderson transition, was proposed by Mott [2] to take the effect of randomness into account.

In this paper we examine the experiments of electric transport [3], static magnetic susceptibility [4] and NMR [5, 6] in phosphorus doped silicon with a purpose to establish a picture for the MNM transition in doped semiconductor.

In addition to the MNM transition, doped semiconductor indicates low temperature anomalies which seem to suggest that transitions to new phases occur at very low temperatures. Mentions will also be given of these phenomena in this paper.

2. Transport experiment on P-doped Si. — In figure 1 two important experimental data in phosphorus doped silicon are reproduced from our earlier work [3]: 4.2 K resistivity and the activation energy $\varepsilon_2$ at 1.2 K as a function of donor concentration $N_D = (eR)^{-1}$, $R$ being the room temperature Hall coefficient.

For samples with $N_D \lesssim 3 \times 10^{18} \text{cm}^{-3}$ the resistivity shows a steep rise with the decrease of $N_D$, while for samples with $N_D \gtrsim 4 \times 10^{18} \text{cm}^{-3}$ the resistivity decreases as approximately $N_D^{-1}$ with the increase of $N_D$.

$\varepsilon_2$ is shown to vanish at $N_D = 3.2 \times 10^{18} \text{cm}^{-3}$. If the transition to metallic state is discriminated by the vanishing of the activation energy, the critical concentration of MNM transition is determined as $3.2 \times 10^{18} \text{cm}^{-3}$ without ambiguity. This value will be referred as $N_D^{*}$. The spatial distribution of impurity atoms is almost statistical in the host semiconductor. Because of the Coulomb repulsion working between the neighbouring impurity ions, too close configuration will be avoided in the melt, and thus a deviation from the statistical

![Fig. 1. Resistivity at 4.2 K and $\varepsilon_2$ activation energy of conduction at 1.5 K versus donor concentration in P-doped Si.](http://dx.doi.org/10.1051/jphyscol:1976454)
distribution of impurities may not be realized in very heavily doped crystals. However, for samples with \(N_D\) around the MNM transition the impurity distribution can be regarded as perfectly statistical, and the spatial fluctuation of the local density of donors is expected according to the statistical law.

In a sample with \(N_D = N_C^{(2)} = 3.2 \times 10^{18} \text{ cm}^{-3}\), the whole crystal is a mixture of regions with relatively high and low local densities of impurity, and metallic channels must be formed through the crystal along the higher density regions.

In places out of the metallic channels there will be various sizes of clusters of donors as well as isolated donors. Here, we mean by cluster a group of donors among which itinerant motion is allowed for the ground state electrons. The size and number of cluster vary with \(N_D\). Even for \(N_D\)'s below \(N_C^{(2)}\), there exists appreciable amount of clusters, however, no percolation of electrons is allowed over a macroscopic size of length.

3. Magnetic Susceptibility Observation of MNM Transition in P-doped Si. — Figure 2 shows the temperature dependence of static magnetic susceptibility \(\chi\) in phosphorus doped silicon [4, 7]. The susceptibility of the pure sample represents the contribution of the host matrix. The most heavily doped sample, with \(N_D = 1.1 \times 10^{19} \text{ cm}^{-3}\), shows a typical Landau-Perel-Pauli diamagnetism of metallic electrons with the Fermi temperature of 200 K. For two samples with \(N_D = 3.3 \times 10^{18}\) and \(4.5 \times 10^{18} \text{ cm}^{-3}\) \(\chi\) is a superposition of LPP diamagnetism and a paramagnetism obeying the Curie-Weiss law. For a sample with \(N_D = 6.5 \times 10^{18} \text{ cm}^{-3}\), \(\chi\) is almost LPP type but a trace of CW type component is seen at lowest temperatures. It should be noted that all the doped samples illustrated in figure 2 are metallic from transport properties.

There is no doubt to consider that the electrons contributing to the metallic conductivity gives rise to the LPP diamagnetism. The CW type component is considered to come from clusters in the nonmetallic places of the crystal.

From the analogy to metallic fine particles [8], following two types of clusters are distinguished by their magnetic property:

i) Clusters consisting of odd number donors: approach to Curie paramagnet with the decrease of donor number and temperature.

ii) Clusters consisting of even number donors: approach to diamagnet with the decrease of donor number and temperature, both i) and ii) approach to LPP magnet with the increase of donor number and temperature.

At very low temperatures the paramagnetic deviation of odd clusters will overcome the diamagnetic deviation of even clusters. Thus, the CW component of observed \(\chi\) for samples with \(N_D = 3.3, 4.5\) and \(6.5 \times 10^{18} \text{ cm}^{-3}\) is attributed reasonably to the cluster of donors in nonmetallic region.

4. NMR Observation of MNM Transition in P-doped Si. — \(^{29}\text{Si}\) and \(^{31}\text{P}\) nuclei are useful NMR probes in P-doped silicon. In addition to the external field \(H\) these nuclei see the contact field \(\Delta H\) of polarized donor electrons. The relative shift \(K\) of the resonance field is given by

\[
K = (\Delta H/H_0) = (8\pi/3)\chi_S |\psi(r_n)|^2.
\]

Here \(\chi_S\) and \(\psi\) are respectively the spin susceptibility and the wave function of donor electrons. \(r_n\) indicates nuclear position. In the present case \(\psi(r_n)\) can be replaced by the envelope of donor wave function.

Spatial variation of \(\psi\) gives rise to an inhomogeneous broadening of resonance line. Isolated donor function has an envelope of 1s character, \(\psi(r) \sim \exp(-r/a_0)\). In clusters and metallic part the wave function of donor electrons will keep its 1s character, but is modulated in phase and amplitude in an irregular way depending on the spatial distribution of donors.

A typical line shape of \(^{29}\text{Si}\) in a metallic sample with \(N_D = 5.1 \times 10^{18} \text{ cm}^{-3}\) is shown in figure 3 [5].

**Fig. 2.** Temperature dependence of static magnetic susceptibility in P-doped Si crystals with \(N_D = 3 \times 10^{17}, 3.3 \times 10^{18}, 4.5 \times 10^{18}, 6.5 \times 10^{18}\) and \(1.1 \times 10^{19} \text{ cm}^{-3}\).

**Fig. 3.** \(^{29}\text{Si}\) NMR spectrum for \(N_D = 5.1 \times 10^{18} \text{ cm}^{-3}\).
The long low field tail of the line reflects the character of the donor wave function. The broadening of the line with the decrease of temperature is observed on both sides of the magnetic field, being explained by assuming the existence of even and odd clusters together with metallic channels. With lowering temperature the line components due to even and odd clusters make respectively diamagnetic and paramagnetic shift while those due to metallic parts makes no shift.

The line shift of $^{29}\text{Si}$ for various samples is shown in figure 4 [5]. A steep rise of the shift for lower $N_D$ and a gradual increase for higher $N_D$ are noteworthy.

With a reasonable assumption that the spin susceptibility $\chi_S$ in eq. [1] is the same for the shift of $^{31}\text{P}$ and $^{29}\text{Si}$, the ratio of the shifts is equal to the ratio of the probability amplitudes of donor electrons at the center and the environs. Figure 6 shows the ratio of peak shifts for $^{31}\text{P}$ and $^{29}\text{Si}$ [5, 6] as a function of $N_D$. When $N_D$ varies from $4.5 \times 10^{18}$ to $5.1 \times 10^{18} \text{ cm}^{-3}$, this ratio shows a steep decrease, indicating that the probability amplitude of donor electrons is decreased at the center and is increased over the environs. This fact suggests that the attractive Coulomb field of donor ions is screened out over a narrow range of $N_D$ around $4.5 \times 10^{18} \text{ cm}^{-3}$. This is consistent with the idea of the Mott transition [1] that the bound state of an electron on an ion disappears at the MNM transition by a cooperative screening of Coulomb field. In doped semiconductor the Mott transition is supposed to take place in a cluster.

$K_p/K_{S1}$ is nearly equal for two samples with $N_D = 5.1 \times 10^{18}$ and $6.7 \times 10^{18} \text{ cm}^{-3}$, while the static magnetic susceptibility curves of these two samples differ drastically. Between these two samples there is little change in screening of donor ion field in spite of rather rapid change in the size of donor clusters. We conjecture that the Mott transition is finished already at $N_D = 5.1 \times 10^{18} \text{ cm}^{-3}$ and further addition of donors results in the increase of the cluster size only.

5. A picture for MNM transition in doped semiconductor. — Summarizing above discussions, the transition to metallic state in doped semiconductor is supposed to occur in two steps, the first step is the local Mott transition making clusters of donors metallic and the second step is the percolation of metalized clusters at $N_C^{(x)}$.

6. Low Temperature Anomaly of Nuclear Spin Relaxation Rate in P-doped Si. — In metallic samples
with \( N_D \) higher than \( 6.7 \times 10^{18} \text{ cm}^{-3} \) and in temperature region above 1.5 K, the relation between the Knight shift and nuclear spin lattice relaxation time \( T_1 \) have been confirmed to satisfy modified Korringa's relation with the electron correlation taken into account [9].

However, for samples with \( N_D \) of \( 2.4 \times 10^{19} \text{ cm}^{-3} \), \( T_1 \) of \( ^{31}\text{P} \) shows an deviation from the Korringa relation at lowest temperatures as shown in figure 7 [6].

\[ T_1 \text{ of } ^{29}\text{Si} \text{ also shows the same deviation [7] with a much longer scale of } T_1 \text{ corresponding to smaller contact field. With fixed temperature } T_1 \text{ is a function of magnetic field, becoming shorter with lowering field [7].} \]

Such an anomaly is consistent with a picture that the metallic donor electrons tend to make a magnetic ordering at a lower temperature \( T_M \) and the spin wave fluctuation above \( T_M \) makes \( T_1 \) shorter. Dotted line in figure 7 is a fit of theoretical result for a case of antiferromagnetic ordering [10, 11] with \( T_M = 0.1 \text{ K} \). Observed magnetic field dependence of \( T_1 \) can be interpreted as the suppression of fluctuation by the external field.

7. Low temperature anomaly of resistivity in Sb-doped Ge. — In Sb-doped germanium \( N_C(\varepsilon) \) is estimated to be around \( 1.5 \times 10^{17} \text{ cm}^{-3} \) [12]. Metallic samples with \( N_D \) up to about \( 1.0 \times 10^{18} \text{ cm}^{-3} \) is known to exhibit anomalous decrease of resistivity when the temperature is lowered below 1 K [13]. Recently this measurement has been extended down to 30 mK [14].

The results is exemplified in figure 8 for a sample with \( N_D = 3.3 \times 10^{17} \text{ cm}^{-3} \). The decrease becomes steeper with the decrease of temperature down to the lowest observed temperature.

Such a temperature dependence can be reproduced by introducing a narrow peak to the scattering relaxation time \( \tau(E) \) at the Fermi level \( \varepsilon_F \), such as a gaussian shown by the insert of figure 8. The curved line in the figure is the resistivity calculated by assuming this \( \tau(E) \).

One interesting point is that this peak of \( \tau \) sticks to the Fermi level by the application of uniaxial stress to cause an intervalley transfer of electrons. The peak of \( \tau \) will be attributed to a scattering mechanism involving many body effect which induces anomaly around the Fermi level. A possible mechanism for this anomaly may be the fluctuating quasi one dimensional superconductivity. Actually, the metallic conductivity in these samples is carried by the percolating quasi one dimensional network of metallic filaments. These filaments are embedded in a medium with high dielectric constant, and the side branches and the clusters situated near the filament have a high electronic polarizability. Such circumstances may be favorable [15] for a fluctuating superconductivity in filaments.

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