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XIII-8. Electron Spin Resonance of Phosphorus Doped Silicon in the Metallic Conduction Region

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An electron spin resonance of phosphorus doped silicon was observed at liquid helium temperatures, and a paramagnetic susceptibility was obtained in the metallic conduction region by comparing the intensity of the resonance line with that of a single crystal of $CuSO_45H_2O$. The paramagnetic susceptibility depends on both temperature and the impurity concentration. The experimental results can be explained reasonably by assuming that the resonance line in the metallic conduction region originates from localized electrons in the system of impurity atoms.

§ 1. Introduction

Since the electron spin resonance on silicon was first reported by Portis *et al.*,[1] most studies have been concerned with the resonance absorption arising from bound donor electrons.[2] We reported in a previous paper[3] that in the low and the intermediate impurity conduction regions the resonance line originates from localized electrons with hopping motion, whose frequency is higher than that of hyperfine interaction.

As the impurity concentration is increased beyond $4\times10^{18}\,\mathrm{cm}^{-3}$, another type of conduction, that is the metallic impurity conduction, takes place.[4] The resistivity and Hall coefficient in this region are nearly constant over the lowest temperatures, which indicates that the conduction electrons form a degenerate Fermi gas. Moreover, a negative magnetoresistance effect similar to that in dilute alloys such as Cu-Mn system[5] was observed in various semiconductors in this region.[4,6] Theoretical[7] and experimental[8] studies on this anomalous effect in germanium suggested the presence of localized magnetic moments in these crystals. Although there has been no direct evidence for the localized magnetic moments, a preliminary experiment of electron spin resonance in this region[9] revealed that samples with the impurity concentration higher than approximately $4\times10^{19}\,\mathrm{cm}^{-3}$ exhibited an anomalous line narrowing at low temperatures, which reminds us of antiferromagnetic resonance near the Néel point. This result strongly suggests that the observed resonance absorption is not due to the conduction electrons. This paper presents the temperature and the concentration dependence of the paramagnetic susceptibility obtained from ESR measurements on phosphorus doped silicon crystals with metallic impurity conduction. The results also suggest that the resonance absorption in these crystals is not due to the conduction electrons. A possibility is presented that the resonance line is due to localized magnetic moments which have been introduced for the explanation of the negative magnetoresistance.

§ 2. Experimental Procedure

The samples were obtained from rods prepared by Czokralski method. Three adjacent slices were cut out from the crystal with 2.5 cm diameter. Samples for ESR measurements were cut out from the middle slice. In order to avoid a distortion of the resonance line due to the skin effect, the samples were made as thin as $10\,\mu$ to $50\,\mu$ by etching technique. The side slices were used for the measurements of Hall coefficient and resistivity, which gave the same result within five percent. The excess donor concentration $n=N_D-N_A$ was estimated from the room temperature Hall coefficient R_H by $n=(eR_H)^{-1}$. An X-band electron spin resonance spectrometer was employed together with 30 c/sec magnetic field modulation and phase sensitive detector systems. The paramagnetic susceptibility was obtained by comparing the intensity of the resonance line with that of a single crystal of $CuSO_45H_2O$. The classical skin depth δ of the samples was calculated to be $5\,\mu$ to $50\,\mu$ in the metallic region. When the thickness of the sample θ is larger than δ, the effective volume of $V(\delta/\theta)$ was used in place of the sample volume V.

§ 3. Experimental Results

3.1. *The number of conduction electrons*

Figure 1 shows the relation between the excess

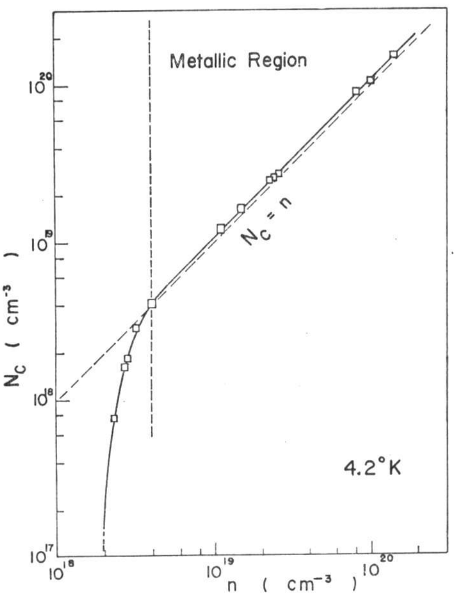

Fig. 1. The relation between the excess donor concentration and the number of conduction electrons obtained from the Hall coefficient at 4.2°K.

donor concentration n and the number of conduction electrons N_c obtained from the Hall coefficient at 4.2°K. $N_c=n$ at concentrations higher than $4\times10^{18}\,\mathrm{cm}^{-3}$, and $N_c<n$ at concentration less than $4\times10^{18}\,\mathrm{cm}^{-3}$. The deviation of N_c from n becomes larger as the concentration is decreased. This result shows that samples become metallic at the concentration of 4×10^{18} cm^{-3}, that is, almost all the donor electrons contribute the electric conduction even at low temperatures.

3.2. The paramagnetic susceptibility

Figure 2 shows the paramagnetic susceptibility χ_p as a function of n at 4.2°K and 1.5°K. The paramagnetic susceptibility shows no abrupt change at the transition between the intermediate and the metallic conduction regions. In the metallic region, the value of χ_p first increases with concentration and attains the maximum at about $2\times10^{19}\,\mathrm{cm}^{-3}$, then decreases with increasing concentration. The concentration where χ_p has the maximum shifts towards lower concentration as the temperature is lowered. Figure 3 shows the temperature dependence of χ_p for several samples in the metallic conduction region. Samples of lower concentrations show an increasing χ_p value as the temperature is lowered. At higher concentrations, on the other hand, χ_p becomes smaller at low temperatures. The temperature, below which χ_p decreases, seems to correspond to that at which the line narrowing occurs.[9)]

§ 4. Discussion

If we adopt an assumption that the resonance absorption may arise from a degenerate electron gas, then the paramagnetic susceptibility of the electron gas in a parabolic band is given by

$$\chi_p=3n\beta^2/2\rho kT_F\,, \tag{1}$$

where n is the carrier concentration, β the Bohr magneton, ρ the density, k the Boltzmann constant and T_F is the degenerate temperature.

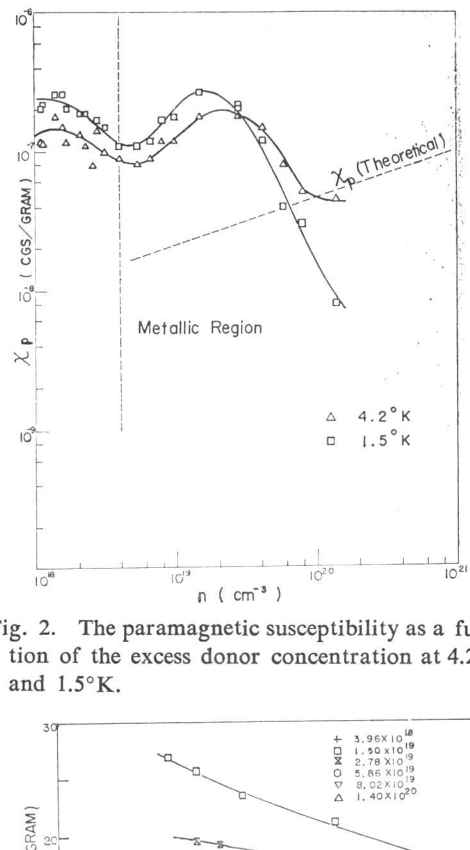

Fig. 2. The paramagnetic susceptibility as a function of the excess donor concentration at 4.2°K and 1.5°K.

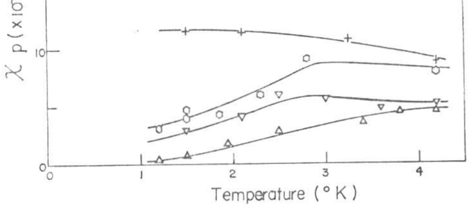

Fig. 3. The temperature dependence of the paramagnetic susceptibility for several samples in the metallic conduction region.

This gives a susceptibility independent of temperature and proportional to $n^{1/3}$, as is shown in Fig. 2.* The contribution from a degenerate electron gas can not explain the temperature dependence of the susceptibility.

Next, we consider another possibility of the origin of the resonance absorption. The negative magnetoresistance effect in these samples suggests the existence of localized magnetic moments. If we assume localized magnetic moments with spin S, then they would give the paramagnetic susceptibility expressed by

$$\chi_p = g^2\beta^2 N_L S(S+1)/3\rho kT\,, \tag{2}$$

where N_L is the concentration of localized magnetic moments. If $S=1/2$ and $g=2$ in eq. (2), it gives, at 1.5°K, $N_L=6\times10^{17}\,\mathrm{cm}^{-3}$ and $1.5\times10^{18}\,\mathrm{cm}^{-3}$ for $n=4\times10^{18}\,\mathrm{cm}^{-3}$ and $1.5\times10^{19}\,\mathrm{cm}^{-3}$, respectively. This shows that there are ten percent localized magnetic moments of the carrier number. Moreover, if S does not depend on temperature or concentration, then N_L is expected to be proportional to the observed value of χ_p. Thus the decreasing behavior of χ_p, or N_L, with decreasing temperature suggests that some localized moments subject to the strong exchange field due to neighboring localized moments will gradually cease to contribute to the resonance absorption around $g=2$. The concentration dependence of χ_p will be related to that of the Knight shift. At the beginning of the metallic conduction region, the Knight shift value of Si^{29} at 1.6°K falls below the extrapolation of the $n^{1/3}$ line from high concentration.[11] The value of this deviation first increases with increasing concentration and attains the maximum at about $1\times10^{19}\,\mathrm{cm}^{-3}$, then decreases. The concentration dependence of the Knight shift deviation is similar to that of χ_p value. This result strongly suggests that the deviation of the Knight shift value from the $n^{1/3}$ relation is due to the presence of localized magnetic moments. At higher concentrations, the number of localized electrons is not appreciable compared with that of conduction electrons, therefore the Knight shift will satisfy the $n^{1/3}$ relation.

* χ_p becomes somewhat larger if exchange and correlation effects are taken into account.[10]

In conclusion, the experimental results can be explained reasonably by assuming that localized magnetic moments contribute to the resonance absorption and there exists antiferromagnetic exchange interaction between these localized magnetic moments.

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DISCUSSION

Winter, J. M.: It seems that your results on paramagnetic susceptibility may be interpreted by taking two facts into account. 1) For concentration lower than 2×10^{19}, correlation effects increase susceptibility and change the concentration dependence. 2) Around $N_d=10^{19}$, the impurity band is merging in the conduction band. There is, therefore maximum and minimum in the density of states, and this fact may explain the anomalous temperature dependence.

Maekawa, S.: Correlation effect and exchange effect make certainly the conduction electron susceptibility somewhat larger as in alkali metal. But, they cannot explain the observed temperature dependence in the degenerate semiconductor. In the metallic like conduction sample, no maximum of the Hall coefficient was observed between 300 and 4.2°K. This suggests that the impurity band and the conduction band cannot be clearly distinguished.

Sasaki, W.: One important point is that the microwave experiment done by Maekawa did show anomaly in susceptibility, while the static measurement have never shown such anomaly.