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Electron-Spin-Resonance Studies of Heavily Phosphorus-Doped Silicon

Hiromoto Ue and Shigeru Maekawa
Electrotechnical Laboratory, Tanashi, Tokyo, Japan
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The paramagnetic susceptibility χ and relaxation time T_1 of phosphorus-doped silicon have been investigated in the temperature range between 1.5 and 100 °K by means of 2- and 9-GHz electron-spin-resonance (ESR) methods. The temperature dependence of χ is found to be appreciable even at temperatures far below the degeneracy temperature for the samples of donor concentrations $4.9 \sim 16 \times 10^{18}$ cm^{-3}, where the metallic-impurity conduction is observed; moreover, in these samples, T_1^{-1} shows a linear temperature dependence. From the analysis of the temperature change of ESR intensities, it is concluded that χ should be composed of two parts: a contribution of the Curie paramagnetism due to *localized magnetic moments* and that of the Pauli paramagnetism of conduction electrons. The donor concentration dependence of each part is in qualitative agreement with the results of the Mikoshiba's inhomogeneity model. The linear temperature dependence of T_1^{-1} is interpreted as due to the interaction between localized moments and conduction electrons, where Hasegawa's theory for dilute alloy systems is applied. The results are also compared with those of the static-susceptibility measurements.

I. INTRODUCTION

The impurity states in heavily doped semiconductors are classified into three groups with regard to electrical transport properties at low temperature[1,2]: low, intermediate, and high concentrations of impurities.

The high-concentration range is also called the region of the metallic-impurity conduction, where the negative-magnetoresistance effect is observed. This effect strongly suggests that localized magnetic moments of some kind should exist in metallic semiconductors.[3,4]

In order to obtain other evidence for localized moment, experiments of electron-spin resonance (ESR)[5] and measurements of static magnetic susceptibility[6] for phosphorus-doped silicon have been carried out from the standpoint that the information on magnetic properties should be essential for this problem. In the ESR measurement, unexplainable and anomalous behavior appeared in the susceptibility-impurity concentration curve, while in the static-susceptibility measurement, Curie-type temperature-dependent susceptibilities associated with localized moments were not observed.

This paper presents the results of the advanced experiment of ESR, where some experimental conditions and procedures of the previous ESR measurement have been modified. In addition to ESR measurement at 9 GHz, we have performed experiments at 2 GHz, where a new method to determine the absolute value of the paramagnetic susceptibility is contrived. The temperature range of measurements has been extended to higher temperatures than that of the previous experiment. In the donor-concentration region 3×10^{18}–2×10^{19} cm^{-3}, direct evidence for localized moments has been obtained from data of ESR intensities. The temperature-dependent part of the ESR linewidth is interpreted as due to the interaction of localized moments and conduction electrons.

II. EXPERIMENTAL

Samples were prepared in the form of powder of diameters 20~ 50 μ by means of crushing and etching techniques developed by Dash.[7] As the measure of the impurity concentration, the Hall concentration N_R was defined by the relation $N_R = (eR)^{-1}$, where e is the electronic charge and R is the Hall coefficient at room temperatures. In the analysis of the data, N_R was assumed equal to the excess donor concentration. The samples are listed in Table I together with N_R and used ESR frequencies. The spectrometer for the 2-GHz ESR was of the reflection type with a coaxial magic tee.[8] The microwave signal was detected by the hot-carrier diode[9] and 30-Hz phase-sensitive detector.

Now we know that the paramagnetic susceptibility χ is expressed by the following equation[10]:

$$\chi = (2\gamma/\pi\omega) \int_0^\infty \chi'' \, dH_0 ,$$

where γ is the gyromagnetic ratio, ω the angular

TABLE I.

Code No.	N_R (cm^{-3})	ESR frequency (GHz)
1	1.5×10^{18}	2
2	3.3×10^{18}	2
3	4.9×10^{18}	2
4	6.1×10^{18}	2
5	1.6×10^{19}	2, 9
6	1.1×10^{20}	9

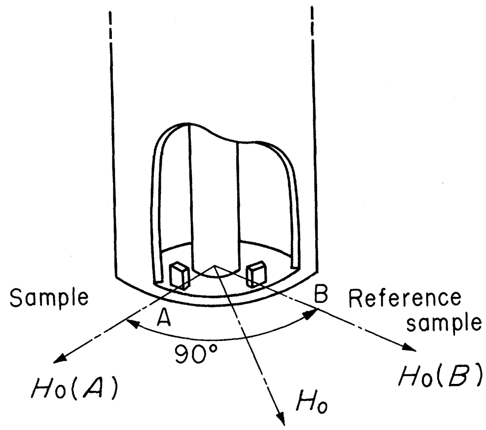

FIG. 1. Configuration of the sample and the reference in the coaxial cavity of TEM_{001} mode for the measurement of the absolute value of the paramagnetic susceptibility.

frequency of the microwave, χ'' the imaginary or loss part of the complex magnetic susceptibility, and H_0 the variable static magnetic field. In order to obtain the absolute value of the paramagnetic susceptibility χ, the integrated area under the curve of the ESR absorption χ'' of the sample should be compared with that of a known amount of the reference sample.

The phase-sensitive-detector outputs of the ESR absorption, after passing through the R-C integrator, were represented on a chart of the recorder; then the planimeter was employed to obtain the integrated areas. Diphenylpicrylhydrazyl (DPPH) is suitable for the calibration purpose because of the linewidth as narrow as that of silicon. On the other hand DPPH has disadvantage that the resonance line overlaps that of silicon because the g value is so close to that of silicon. When a coaxial sample cavity is used as in the case of 2-GHz ESR, however, this drawback can be removed as follows. As is shown in Fig. 1, the sample and the reference sample are mounted at the positions A and B, respectively, in the coaxial sample cavity. In this configuration, the rf magnetic fields for the mode of TEM_{001} at A and B are perpendicular to each other. Resonance signals of the sample and the reference one are separately obtained by turning the direction of static magnetic field H_0 by 90° without changing any other experimental conditions. In Fig. 2, typical resonance lines of the sample and the reference are shown.

III. SUSCEPTIBILITY

The observed paramagnetic susceptibility χ as a function of N_R and temperature T is represented in Figs. 3 and 4.

Figure 3 is a plot of χ at several temperatures against N_R. The variation of χ with temperature is remarkable for the sample at the low-concentration end. In the low-concentration region, the electrons are localized in impurity sites, so that the Curie paramagnetism is expected. In the intermediate and the metallic-impurity conduction region, where the Hall effect is observable at liquid-helium temperatures, electrons will be free to move and the Pauli paramagnetism should be expected. Temperature dependence of χ, however, is appreciable also for the samples in these regions. But such tendency gradually decreases with increase of N_R; finally, for the sample of $N_R = 1.1 \times 10^{20}$ cm^{-3}, χ is independent of T. At concentration below 1.6×10^{19} cm^{-3}, all the curves at each

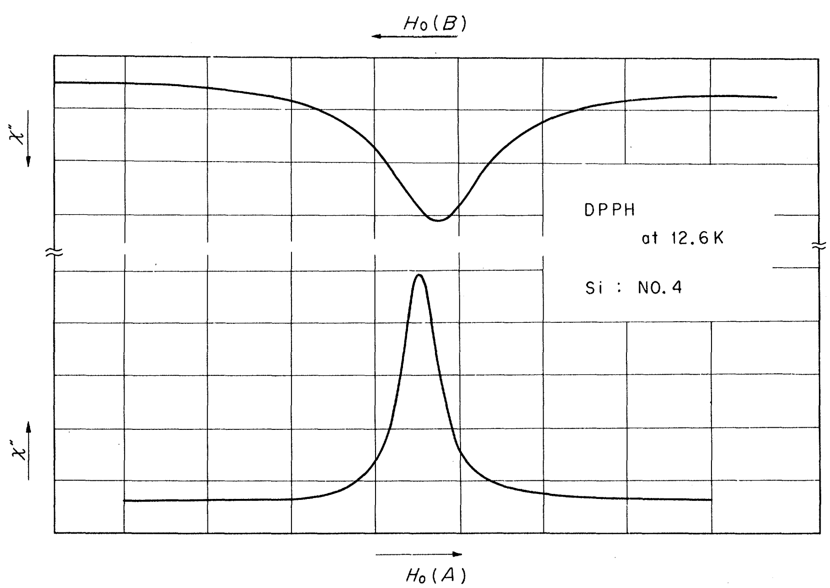

FIG. 2. Typical example of ESR absorption lines of the sample and the reference after passing through the R-C integrator. The scales of χ'' and H_0 of DPPH and Si are same but arbitrary.

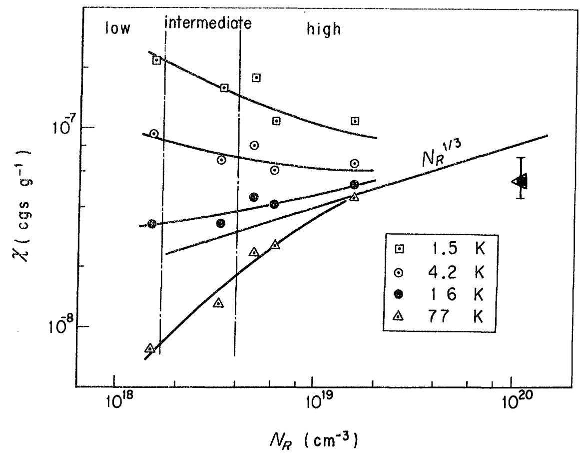

FIG. 3. Concentration dependence of paramagnetic susceptibility χ in emu at several temperatures.

temperature have a tendency to converge into the $N_R^{1/3}$ line. For the sample of $N_R = 1.1 \times 10^{20}$ cm^{-3}, χ is far below the line, which will be discussed later in Fig. 6. For the sample of $N_R = 1.6 \times 10^{19}$ cm^{-3}, both 2- and 9-GHz ESR for powder were measured but no marked difference of the susceptibility was found within experimental errors. Though, in previous data at 9 GHz,[5] there was an anomalous peak at $N_R = 2 \times 10^{19}$ cm^{-3} in χ-N_R curve, no such anomaly has been found in this experiment.

In Fig. 4, ESR measurements of χ against T for all the samples are shown. Sample No. 1 of the low-concentration region shows the behavior of the modified Curie paramagnetism[11] at low temperatures. We consider that the sample No. 6 exhibits the Pauli paramagnetism of the conduction electrons in the degenerate state. In samples 2–5, which belong to regions of intermediate concentration and beginning of high concentrations, it is remarkable that χ increases with falling temperature from high-temperature range; and after the rate of the increase reduces once, χ increases more steeply. In other words, we can see a plateau in the middle-temperature range. When our attention is confined only to this region except for low-temperature side, it might be concluded that the temperature dependence of χ is similar to that of the Pauli paramagnetism. However, it seems rather surprising that the χ values should show temperature dependence even at liquid-helium temperature, where the state of electrons should be degenerate. The increase of χ at these temperatures should be interpreted as due to the contribution other than Pauli paramagnetism. From the behavior of temperature dependence of χ with the change of N_R as shown in Fig. 3, it is natural to conclude that there exists the Curie paramagnetism even in the intermediate- and the high-concentration region, and that its contribution decreases with increasing N_R. We put on the fundamental assumption that χ should be the sum of the contributions from the Curie paramagnetism χ_d and from the Pauli paramagnetism $\chi_s(T)$, i.e.,

$$\chi = \chi_d + \chi_s(T), \quad \chi_d = (n_d \mu_B^2/\rho k) T^{-1} ,$$
$$\chi_s(T) = \chi_s(0) \tfrac{2}{3} (F'/F)(T/T_D)^{-1} , \qquad (1)$$

where n_d is the spin concentration associated with the Curie paramagnetism, μ_B the Bohr magneton, ρ the density of silicon, k the Boltzmann constant, $\chi_s(0)$ the susceptibility due to the Pauli paramagnetism at $T = 0\,°$K, F and F' the Fermi integral and its derivative, respectively, and T_D the degeneracy temperature. Choosing n_d and $\chi_s(0)$ as adjustable parameters and fixing T_D as calculated from N_R and band parameters, we can fit the above-mentioned χ value to the measured one. The dotted lines in Fig. 4 represent the χ_d and $\chi_s(T)$ values and the solid line is the sum of these two contributions. Clogston *et al.*[12] measured the magnetic susceptibility of alloys containing iron atoms and divided it into two parts, i.e., the temperature-dependent part and the constant one. From the value of the former, which corresponds to the Curie-Weiss law, the magnetic moment of an iron atom was decided. In our case, the same procedures are followed, but for simplicity the Curie law is taken instead of the Curie-Weiss law and the g and the S values are assumed to be 2 and $\frac{1}{2}$, respectively.

The n_d and the $\chi_s(0)$ values obtained from this analysis are plotted against N_R in Figs. 5 and 6, respectively. In Fig. 5, it is found that n_d decreases with increasing N_R and becomes nearly zero at $N_R = 1.1 \times 10^{20}$ cm^{-3}.

Toyozawa's theory[4] describes the state of localized magnetic moments in the metallic semiconductors on the basis of the calculation of the impurity band by Matsubara and Toyozawa[13] and Anderson's criterion[14] of the appearance of the localized moments in dilute alloy systems. The results of this theory are in qualitative agreement with many features related to the negative magnetoresistance effect. The n_d values due to this theory, however, should increase with increasing N_R not in accordance with the present experiments. Mikoshiba[15] proposed a simple *inhomogeneity model*, in which the impurity states are regarded as spatial mixtures of the metallic and the nonmetallic region. He used the Poisson distribution of impurities and the critical distance between impurities in the Mott transition.[16] The theoretical curve in Fig. 5 due to this model, with effective Bohr radius taken as 18 Å, is in qualitative agreement with experimental points.

As to the $\chi_s(0)$ values in Fig. 6, experimental points obey the $N_R^{1/3}$ relation in the Hall-concentration region between 5×10^{18} and 1.6×10^{19} cm^{-3}, but

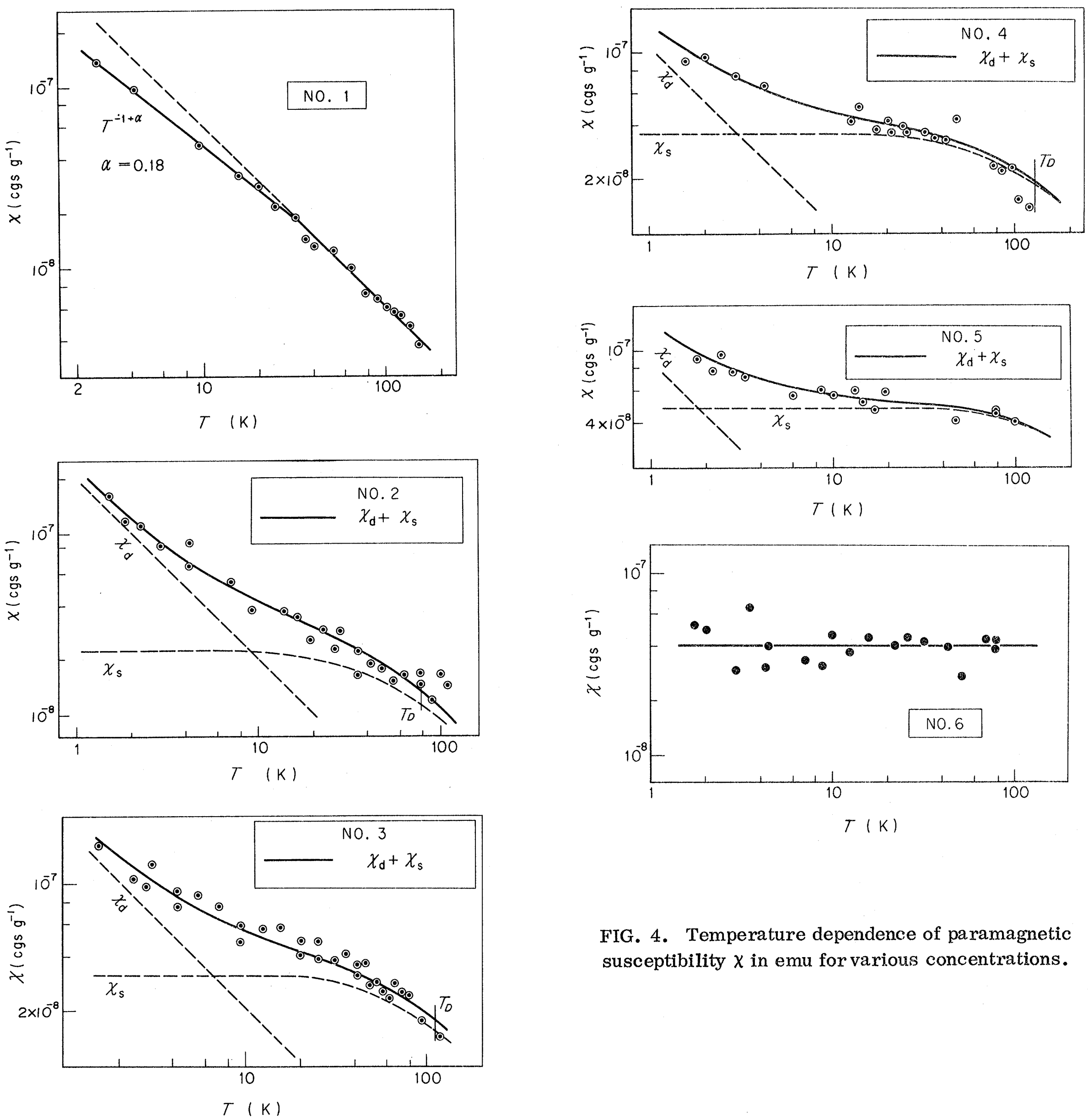

FIG. 4. Temperature dependence of paramagnetic susceptibility χ in emu for various concentrations.

outside this region experimental values deviate from the extrapolated curve of the $N_R^{1/3}$ relation. Theoretical curve of the inhomogeneity model is represented by the solid line, which is equal to the Pauli paramagnetism above $N_R = 1.5\times 10^{19}$ cm^{-3}. In this theory, it is assumed that in the metallic region the electronic state can be described by a degenerate Fermi gas in a band with the same band parameters as the conduction band. The experimental values show similar behavior to that of the theory below $N_R = 1.5\times 10^{19}$ cm^{-3}, but they are different from each other by a factor of about 2. Pines's theory,[17] which treats the electron-electron interaction on paramagnetic susceptibility of conduction electrons in metals, suggests that enhancement factor of the Pauli paramagnetism is about 1.3. It seems that effects of the electron-electron interaction and the perturbing impurity potential might be responsible for this large enhancement factor. For sample No. 6, $\chi_s(0)$ deviates far from the extrapolated value of the $N_R^{1/3}$ relation. In this concentration, the mean distance between impurities is smaller than the effective Bohr radius of the donor electron, so that the effect of the perturbing impurity potential is expected to influence paramagnetic susceptibility, and higher-band effects might also play an important role.

Let us compare our results with static-susceptibility measurements,[6] in which the sum of the diamagnetic and the paramagnetic contributions is measured. In the static-susceptibility measurement the contribution from the Curie paramagnetism is hardly observed in the metallic-impurity conduction region. The fact that the result of ESR at 9 GHz is the same as that at 2 GHz for sample No. 5 indicates that there does not exist nonlinearity of paramagnetic susceptibility associated with magnitude of static magnetic field, so that the difference in the results of the ESR measurement from that of the static measurement cannot be attributed to the nonlinear susceptibility. Mikoshiba suggests that the paramagnetic part of the nonmetallic region will be cancelled by the diamagnetic part of that region for the case of antimony-doped germanium at $T = 1.24\,^\circ$K. However in our case, for instance at $N_R = 6.1\times 10^{18}$ cm^{-3}, this cancellation will take place at about 25 °K; then at liquid-helium temperatures large contribution of Curie paramagnetism should be observed in the static-susceptibility measurement, so that this suggestion is not appropriate to our case. A possibility that the resonance absorption due to surface defects in a powdered silicon has been observed in our ESR experiments seems remote because, though samples 1–6 were made with identical method, systematic N_R dependence of χ was obtained. On the basis of above considerations it should be concluded that there exists the temperature-dependent diamagnetism which would cancel the Curie paramagnetism in the beginning of the metallic-impurity conduction region. If this assumption is adopted, the temperature-independent diamagnetism χ_{dia} at low temperatures can be estimated by subtracting $\chi_s(0)$ from the static susceptibility at low temperatures.

In Fig. 7, χ_{dia} obtained with this procedure against N_R is shown. Experimental points are on

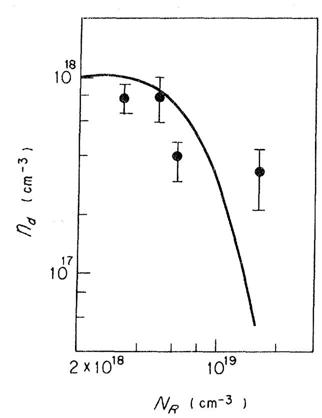

FIG. 5. Concentration dependence of the n_d values. The theoretical curve is due to Mikoshiba's inhomogeneity model with effective Bohr radius of 18 Å.

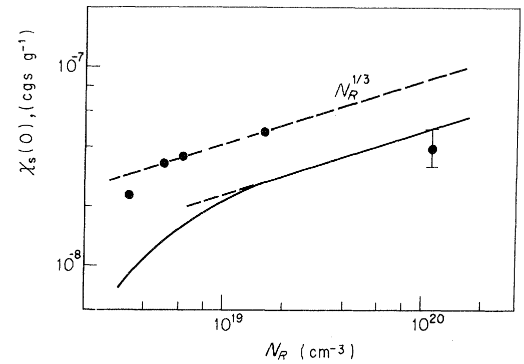

FIG. 6. Concentration dependence of the $\chi_s(0)$ values. Theoretical curve due to the inhomogeneity model is represented by the solid line.

the $N_R^{1/3}$ line in the vicinity of $N_R = 10^{19}$ cm^{-3}. Outside this region they deviate from this line as does the case of $\chi_s(0)$. The inhomogeneity model could qualitatively explain the behavior of χ_{dia} seen in the lower-concentration region. The solid line due to this model is the sum of the diamagnetic susceptibility of the metallic region and that of the nonmetallic region. This theoretical diamagnetic susceptibility is equal to the Landau-Peirls diamagnetic susceptibility above $N_R = 1.5\times 10^{19}$ cm^{-3}. The trend that the absolute value of χ_{dia} experimentally obtained is smaller than the theoretical value has been also observed for n-type germanium by Bowers.[18] The large deviations of the measured values from the theoretical one in the vicinity of $N_R = 10^{20}$ cm^{-3} possibly would be interpreted as due to effects of the electron-electron interaction and the perturbing impurity potential; it also would be possible that the effect from higher bands might play an important role as has been pointed out in the case of InSb.[19]

IV. LINEWIDTH

Figure 8 is a plot of the linewidth δH_{ms} against T

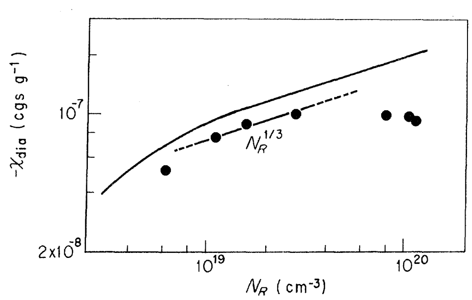

FIG. 7. Concentration dependence of the temperature-independent diamagnetism χ_{dia} at low temperatures obtained from the subtraction of $\chi_s(0)$ from the static susceptibilities. Theoretical curve is due to the inhomogeneity model.

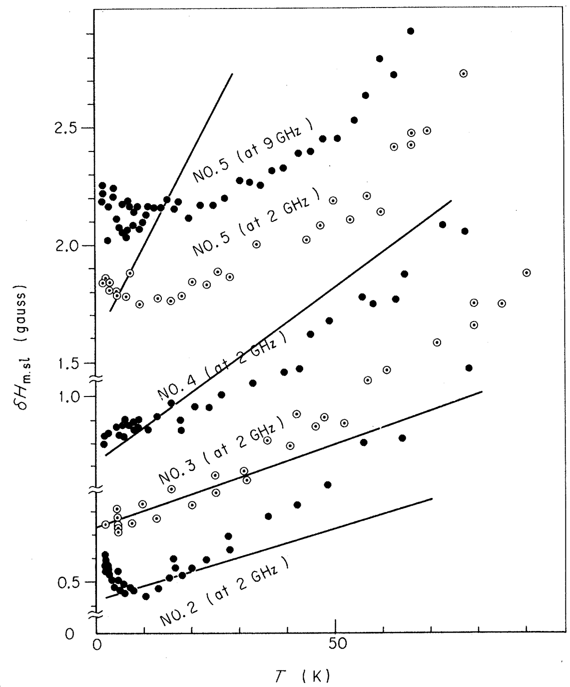

FIG. 8. Temperature dependence of the linewidth for samples of intermediate and metallic-impurity conduction regions. Solid lines are due to Hasegawa's theory.

for the samples 2~ 5, where δH_{ms} is the width between points of maximum slope of the Lorentzian absorption line. Except for samples 2 and 5, a monotonic increase of δH_{ms} with increasing T can be observed. At liquid-helium temperatures, δH_{ms} increases with increase of N_R in this impurity-concentration region.[20] For sample No. 5, both experimental values at 9- and 2-GHz ESR are shown; a constant difference at all the measured temperatures is found.

The temperature-dependent part of the linewidth or the relaxation rate shows a linear temperature dependence. According to Yafet's theory,[21] the spin-lattice relaxation rate T_1^{-1} of the conduction electrons for silicon is proportional to the T^5 law at $T \ll T_D$. From the results of our susceptibility measurements, it has become clear that there exist not only conduction electrons but also localized moments in the heavily doped silicon, so that interaction between these two spin systems is expected to affect the ESR linewidth. Now, it is assumed that Hasegawa's theory,[22] which treats dynamical properties of two spin systems composed of conduction-electron spins and localized d spins interacting by exchange, could be applied to our case. According to this picture, the effective relaxation rate is represented by

$$T_{1,\mathrm{eff}}^{-1} = T_{s1}^{-1}\chi_r^{-1}, \quad \chi_r = \chi_d/\chi_s(0) \tag{2}$$

where T_{s1}^{-1} is the spin-lattice relaxation rate of the conduction electrons. The susceptibility ratio χ_r is inversely proportional to T. This relation is established in the case of dilute alloys.[23-25] In our case, the relaxation rate T_{s1}^{-1} can be estimated from Elliott's theory,[26]

$$T_{s1}^{-1} = \tau_R^{-1}(\Delta g)^2(N_R/5.0\times 10^{22})^{2/3}, \quad \Delta g = 3.5\times 10^{-3} \tag{3}$$

where τ_R is the relaxation time characteristic of electrical resistivity and can be estimated from the Hall mobility[2] and Δg is the *g shift*.[27,28] The susceptibility ratio χ_r could be obtained from our experimental data. The solid lines in Fig. 8 are due to this procedure and show rather good agreement with experiments except for sample No. 5, in which the temperature coefficients are different from each other by a factor of 3.

In sample Nos. 2 and 5, the broadening of the linewidth with lowering temperature is found. Sample No. 1, which belongs to the low-concentration region, also shows line broadening with decreasing temperature; this behavior could be understood as the effect of the motional narrowing due to the hopping motion of electrons in the nonmetallic region.[20] Since sample No. 2 belongs to the intermediate-concentration region, there exist some nonmetallic regions large enough to contain more than two donors, where the hopping motion might be possible. The line broadening of sample No. 2 would be due to this kind of the hopping motion.

The line broadening for sample No. 5 is quite anomalous and no explanation is found. This problem is left for future study. The linewidth of sample No. 6 at 9 GHz was recognized to increase from 16 to 19 G with increasing temperature from 2 to 80 °K. But we could not get a good signal-to-noise ratio for discussing the temperature dependence of the linewidth accurately.

V. CONCLUSION

Intensities of ESR and the relaxation time T_1 of the heavily phosphorus-doped silicon have been investigated. It was concluded from the data of ESR intensities that the spin systems observed in ESR are the localized magnetic moments and the conduction electrons in the region of the metallic-impurity conduction and the temperature dependence of T_1 supports this picture. The donor-concentration dependence of both susceptibilities due to these two spin systems was in qualitative agreement with the inhomogeneity model proposed by Mikoshiba.

Note added in manuscript. After this paper was submitted for publication, an article by J. D. Quirt and J. R. Marko [Phys. Rev. Letters 26, 318 (1971)] appeared. Employing the modulation-switch technique, they obtained the constant-temperature relative χ value of the P-doped Si at 1.1, 4.2, and 77 °K, which is essentially in agreement with the present result. However, because of the lack of (a) a detailed analysis of the temperature dependence of χ and (b) the absolute determination and comparison with the static values, their discussions on localized-moment problem remain rather speculative.

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Light Scattering from Polaritons and Plasmaritons in CdS near Resonance

Jagdeep Shah, T. C. Damen, J. F. Scott,* and R. C. C. Leite†
Bell Telephone Laboratories, Holmdel, New Jersey 07733
(Received 4 January 1971)

We have investigated light scattering from polaritons and plasmaritons in CdS near resonance. These results are compared with computer-calculated dispersion curves for these excitations. We find a good agreement between theory and experiments. Particular attention is given to interesting effects arising from birefringence and resonance.

I. INTRODUCTION

It is well known[1] that there is a strong coupling between the transverse optical (TO) phonons in polar crystals and electromagnetic waves when their energies and wave vectors are nearly equal. The coupled photon-TO mode, known as the "polariton," has been investigated in a number of crystals by light scattering at small angles.[2] However, light scattering from polaritons in CdS has not been reported so far.

The polariton dispersion relation in a crystal is