Effects on the NMR Properties of the Metal–Nonmetal Transistion in Impure Semiconductors

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The nuclear relaxation of ^{29}Si in phosphorus-doped silicon is studied from the metal–nonmetal transition point of view. Going from the nonmetal to the metal there is a rapid decrease of relaxation time at the transition, donor impurity $\approx 10^{18}$ P atoms/cm^3. For the insulating side of the transition the dominant process of relaxation is due to the modulation of the dipolar interaction between the impurity electron spin hopping from one impurity center to another, and the nuclear spins. This type of relaxation can only take place if the material is compensated. For the metallic side of the transition the dominant process of relaxation is due to the modulation of the hyperfine coupling between the nuclei and the highly degenerate electron gas in a narrow band. The electron density in the vicinity of the donor centers is measured in a 2.5×10^{18} P atoms/cm^3 sample. The measurement shows that it remains strongly localized around the impurities. A comparison is made of our results with the D^- band model of conductivity.

I. INTRODUCTION

It has been known for some time now that the varying of the concentration in heavily doped semiconductors causes a transition from a nonconducting phase, "nonmetal," to a conducting phase, "metal." The most striking evidence of a metal–nonmetal transition is found in the study of the conductivity and Hall effect in doped germanium or silicon.[1–3]

At low concentration of donor impurities the overlap between the wave functions of close neighbors is negligible and the number of free carriers at $T=0$ is zero. At high concentration of donor impurities the overlap is no longer negligible and consequently the electrons move freely in a narrow band which may sometime overlap the bottom of the conduction band.

The transition between these two distinct phases occurs at a concentration N given by the Mott criterion, in a sharp range of concentrations:

$$N^{1/3}a_{\mathrm{H}}\approx 0.2, \tag{1}$$

where a_{H} is the Bohr radius for the impurity

The aim of this work is to study the spin–lattice relaxation time of ^{29}Si nuclei in phosphorus-doped silicon for both sides of the metal–nonmetal transition. At concentrations of impurities lower than 10^{17} P atoms/cm^3 in Si:P,[4] the EPR spectrum is composed of two hyperfine components which are due to the spin $\frac{1}{2}$ of the phosphorus nucleus. Between 10^{17} and 10^{18} P atoms/cm^3 there is a decrease in the intensity of the hyperfine components together with a growth of the central line. At the concentration 2.5×10^{18} P atoms/cm^3 the EPR spectrum consists of a very narrow homogeneous line at 1.3°K. The spectrum then looks very much like a conduction electron line in a metal with a g factor of 1.99875.[5] It is thought that the fast movement of the electrons all over the crystal washes out the hyperfine interaction with the phosphorus spins. On Fig. 1 we have shown the relaxation times we measure versus concentration at various temperatures. We first have to propose a model for the relaxation in the 10^{17} P atoms/cm^3 range (or nonmetallic side of the Mott transition) and then look at the range of 2.5×10^{17} P atoms/cm^3 (or metallic side of the Mott transition).

II. NONMETALLIC PHASE

The model we propose for the ^{29}Si relaxation is based on a hopping process. By this we mean the tunneling of an electron from a neutral donor to an ionized neighbor.[6] Some compensation is needed for this mechanism to be efficient. We call N_{D} and N_{A} the concentration in donor and acceptor centers, respectively.

Let us consider a ^{29}Si nucleus located in the vicinity of a pair of donors (neutral–ionized phosphorus). The dipolar magnetic field "seen" by the ^{29}Si spin and due to the electron spin S of the pair is written as follows:

$$\mathbf{H}_{\mathrm{dip}}=(\hbar\gamma_e/r^3)\{\mathbf{S}-3(\mathbf{r}/r)[\mathbf{S}\cdot(\mathbf{r}/r)]\},$$

where $\mathbf{r}$ is the vector joining the electron and nuclear spins. The hopping of the electron by absorption or emission of a phonon makes this field random. We have calculated from the hopping frequency of the Miller and Abrahams theory[6,7] the correlation time τ for the perturbation. This procedure gives a rate of relaxation $1/T'_1(r)$ for a ^{29}Si nucleus close to a fast-relaxing center. We have also assumed that the nuclear magnetization is propagated from and to the relaxing centers through a spin-diffusion mechanism in the

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^{29}Si random lattice. Finally we get a unique relaxation time T_1 for the magnetization which depends on the applied magnetic field H, the acceptor concentration, and the donor concentration. When τ is long compared to the Larmor period of the nuclear spin, the dependence is as follows:

$$1/T_1 \approx (N_A/H^{1/2}) \exp(-d/2a_H), \qquad (2)$$

where d is the mean distance between donor centers given by

$$(4\pi d^3/3)N_D = 1.$$

The above derivation is arrived at after an averaging process which takes into account the random distribution of the impurities. In order to check the N_A dependence of Eq. (2), experiments on compensated samples have been done ($N_D = 6\times10^{16}$ P atoms/cm^3, N_A/N_D = 0.13; 0.33; 0.67). Some results are presented in Fig. 2. The magnetic-field dependence agrees quite well with our theory. We believe that even for the supposed noncompensated samples, the results of which are reported on Fig. 1, the relaxation could be due to the existence of a residual compensation ($N_A/N_D \approx 5\%$). The fast variation of the relaxation time against a mean distance between donors is due to the exponential factor in Eq. (2).

III. METALLIC PHASE

On the metallic side of the Mott transition we have studied the ^{29}Si relaxation in the domain 10^{18} to 10^{19} P atoms/cm^3, Fig. 1, but we have done a more complete analysis of the properties of the 2.5×10^{18} P atoms/cm^3 sample. As we said above, the donor

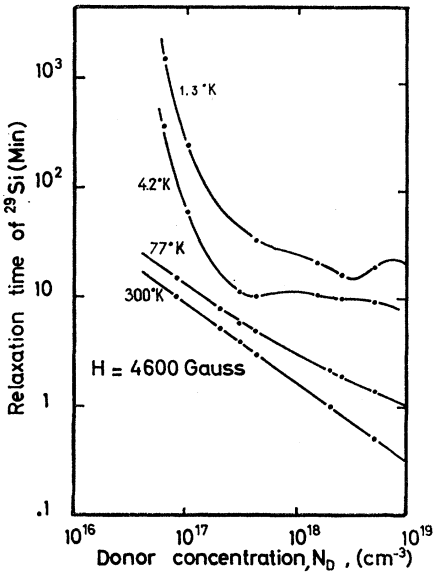

FIG. 1. Relaxation time in Si:P as a function of concentration at different temperatures in a magnetic field of 4600 G.

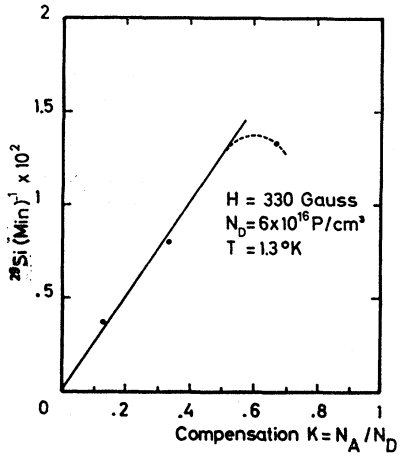

FIG. 2. Rate of relaxation of boron-compensated samples with a donor concentration of 6×10^{16} P atoms/cm^3.

electrons are delocalized. The contact term of the hyperfine interaction between the spins of the electrons and the spins of the nuclei at the distance r from a center is written as follows:

$$\hbar\mathcal{H}(r) = -(8\pi/3)\gamma_e\gamma_r\hbar^2\delta(r)\mathbf{I}\cdot\mathbf{S}. \qquad (3)$$

In an applied magnetic field the interaction (3) shifts the Larmor frequency ν_0 for the nuclei $\{r\}$ by an amount $\Delta\nu(r)$ and provides an effective spin–lattice mechanism $T_1'(r)$. $\Delta\nu(r)$ and $T_1'(r)$ are not independent quantities but are related through the Korringa relation[8]

$$T_1'(\Delta\nu/\nu_0)^2 = (\pi kT)^{-1}(N/\rho_F)^2(\langle S_z\rangle^2/\gamma_n^2\hbar H^2). \qquad (4)$$

The counterpart of the Knight shift $\Delta\nu(r)$ is the shift of the electron Larmor frequency which is characterized by the local magnetic field $\mathbf{H}_n(r)$. The latter is proportional to the mean magnetization of the nuclei $\{r\}$, $\langle I_z(r)\rangle$, and to the local electron probability density $|\psi(r)|^2$. We do not go into the details of a sophisticated experimental method[4,9] which gives us the relaxation $T_1'(r)$ for the nuclei of which the Larmor frequency is $\nu_0+\Delta\nu(r)$, see Fig. 3. The shift $\Delta\nu(r)$ is proportional to $|\psi(r)|^2$ and takes an appreciable value for nuclei very close to the impurities ($r \ll d$). One can also show[9] that the hyperfine interaction (3) is the only effective interaction between the spins and the lattice. The spin diffusion is ineffective in propagating radially the magnetization between close-neighboring nuclei for which the local-field variation is larger than the spin–spin dipolar interaction. But, as we have shown,[9] the spin diffusion becomes very effective for nuclei located far from any impurity and gives the relaxation time T_1 for the global magnetization, Fig. 1. At temperature $T \lesssim 4.2$°K we have found that $1/T_1$ is proportional to

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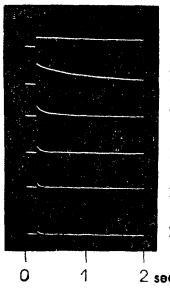

FIG. 3. Relaxation associated with a definite Knight shift for nuclei close to the impurities ($N_D = 2.5\times10^{18}$ P atoms/cm^3) [after Ch. Ryter (private communication)].

T, as it is in a metal with a strongly degenerate electron gas.[8] A direct measurement of the electron susceptibility χ by EPR had been performed in the 2.5×10^{18} P atoms/cm^3 sample and can be compared to the measured Pauli susceptibility. The value of the ratio χ/χ_{Pauli} is 2.9 and is greater than the value of alkaline metals ($\approx$1.8). One might interpret this result as strong correlation effects among electrons in the narrow band.[10]

IV. DISCUSSION

The critical concentration in impurities which is derived from the Mott criterion (1) is 2×10^{18} P atoms/cm^3, where $a_H = 16.3$ Å is the value given by ionization-energy measurements. Our results seem to corroborate the Mott criterion. On the one hand, for $N_D \approx 10^{17}$ both the EPR spectrum and the ^{29}Si relaxation suggest that the only movement of the electrons is accomplished by a hopping mechanism requiring an activation energy. On the other hand, we have shown that at a concentration of 2.5×10^{18} P atoms/cm^3 the nuclear spins interact strongly with a degenerate electron gas. This electron gas is nonlocalized though it remains strongly peaked in the vicinity of the impurity centers. The electron probability density for the nuclei far from the impurities remains at a value much lower than it would have been if the electrons were thermally excited into the conduction band.[11] In several papers the conductivity of antimony-doped germanium had been carefully studied in the region of the metal–nonmetal transition.[1,3,12] Different activation energies for the conductivity process have been found. The one we are presently interested in is the energy ϵ_2 which, in the nonmetallic phase, decreases rapidly and without discontinuity to a zero value at a concentration in donor centers verifying the Mott criterion (1).[13] It has been suggested that the energy ϵ_2 is associated with the activation of an electron from a neutral donor to the band D^- formed by interacting negatively charged donors.[14] The band picture would be the one given[13] where the narrow D^- band is below the conduction band.

One suggestion we can make is that the band we have found, through magnetic measurements, in a 2.5×10^{18} P atoms/cm^3 sample is the same as the D^- band of conductivity. These results do not conflict with the work of Sundfors and Holcomb,[15] who have shown by NMR that for concentrations greater than 3×10^{19} P atoms/cm^3 the electrons can be described by a highly degenerate gas and that the shape of the band is parabolic. The band is likely to be the bottom of the conduction band.

ACKNOWLEDGMENTS

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Discussion of Jérome's Paper

G. J. HYLAND (The University of Liverpool): I would like to ask a question concerning the interpretation of the Knight shift and the susceptibility of these impurity bands. Do you think the Kubo temperature-independent paramagnetism can play a role in this case? This, of course, is only possible if there is an orbital degeneracy in the band.

D. JÉROME: I must say that in fact, as Dr. Holcomb says, it is very difficult to extract a good result for the spin susceptibility from the ESR measurement. We compared the electron line with a salt for calibration. But I think one shouldn't trust too much this kind of result, especially at low temperature. In the interpretation of the data, we did not take into account the possibility of a Kubo mechanism.

D. F. HOLCOMB (Cornell University): I just wanted to make one comment to emphasize how Dr. Jérome's measurements connect on to some of the comments I made in the previous talk. Namely, with this rather elegant, double-resonance technique, one measures the nuclei near the phosphorus impurity and sees a situation in which the Korringa relation is maintained. Whereas if one does a bulk measurement, that is just the region in which one sees the bulk Knight shift dropping below proportionality to $N_D^{1/3}$, so that by putting those two measurements together one sees that, in the bulk far away from the phosphorus, in the impurity-band regime, the electrons do not have strong coupling to the nuclei, but when you get close to the donor you see something that looks very much like metallic coupling.

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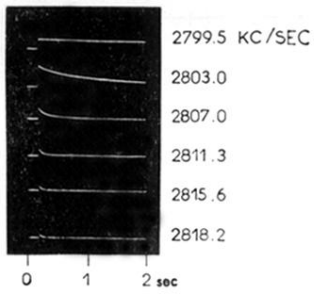

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