

Title	Hyperfine Interactions of Short-Lived 12B in Si Crystal
Author(s)	Izumikawa, Takuji
Citation	大阪大学, 1999, 博士論文
Version Type	VoR
URL	https://doi.org/10.11501/3155539
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# Hyperfine Interactions of Short-Lived <sup>12</sup>B in Si Crystal

THE OSAKA UNIVERSITY GRADUATE SCHOOL OF SCIENCE TOYONAKA, OSAKA

Takuji Izumikawa

DISSERTATION IN PHYSICS



# 0

# Hyperfine Interactions of Short-Lived <sup>12</sup>B in Si Crystal

Graduate School of Science Osaka University Toyonaka, Osaka, Japan

Takuji Izumikawa

Dissertation in Physics, 1999

# Abstract

The lattice locations of boron atom implanted in the semiconductor Si were studied by detecting  $\beta$ -NMR using the polarized  $\beta$ -emitter <sup>12</sup>B. While the B atom is one of the typical dopants in Si, little has been known rigidly about the location of implanted B except for the substitutional site and the temperature dependence of its fraction. Moreover, in the previous  $\beta$ -NMR studies there was a missing fraction (~30 %) of implanted B and were some contradictions even in the fraction of the substitutional B. The purpose of the present study is to investigate the locations of the implanted B and their fractions as a function of temperature through the careful detection of the  $\beta$ -NMR in order to understand the behavior of B atoms in Si.

lattice sites and obtained their fractions.

It has been known before the present study that the main fraction of <sup>12</sup>B is located in the substitutional  $(B_s)$  site and some fraction is located in a nonsubstitutional  $(B_{ns})$ site with (111) axial symmetry. In addition to these two sites, we found in the present study a broad resonance around the Larmor frequency, which we call the B<sub>x</sub> site. Thus, at the temperature below 260 K, all the fractions of the implanted <sup>12</sup>B were made clear without any missing fraction.

The fractions of these three different sites were measured as a function of temperature in a range from 100 K to 800 K. Two remarkable results were obtained; (1) the B<sub>ns</sub> nuclei become undetectable suddenly at 260 K and above; (2) while the sum of the fractions  $(B_s + B_x)$  is constant from 100 K to 450 K, the fraction increases to 100 % above 450 K. The steep decrease of  $B_{ns}$  fraction is caused by a thermal jump of the  $B_{ns}$  atom between the identical locations, *i.e.*, the fluctuating electric field gradient due to the thermal jump causes the fast spin-lattice relaxation of the nuclear polarization of <sup>12</sup>B

The polarized <sup>12</sup>B nuclei were produced through  ${}^{11}B(d, p){}^{12}B$  reaction with the deuteron of 1.5 MeV and with restricting the recoil angle of about 40°. The <sup>12</sup>B was implanted in a Si sample, whose temperature was kept constant, placed with its (110) axis set parallel to the applied magnetic field of 6.000 kOe. Then applying rf and detecting  $\beta$ -ray from <sup>12</sup>B nuclei, we observed the NMR of the <sup>12</sup>B in Si. Three Si samples with different densities of dopants were prepared  $(3 \times 10^{14} \text{ B/cm}^3, 7 \times 10^{17} \text{ B/cm}^3, 6 \times 10^{14} \text{ B/cm}^3)$  $P/cm^3$ ). From the resonance frequencies and NMR amplitudes, we distinguished the in  $B_{ns}$  sites. Assuming the Arrhenius behavior of the thermal jump, the jump rate of the  $B_{ns}$  was deduced based on the  $(B_{s}$ - Si<sub>i</sub>) pair model for the atomic configuration which was predicted theoretically to be most probable. The obtained jumping rate is (2.5  $\times 10^{9}$ ) exp $(-0.47\pm0.04(eV)/kT)$  kHz ( the error of the pre-exponential factor is  $+6\times10^{9}$ ,  $-1.5\times10^{9}$ ). As well as the decrease of the  $B_{ns}$  fraction, the recovery of the <sup>12</sup>B fraction in the  $B_{s}$  site or the  $B_{x}$  site above 450 K is successfully understood by the dissociation of  $(B_{s}$ - Si<sub>i</sub>) pair with the dissociation rate of  $5 \times 10^{9} \exp(-0.84 \pm 0.06(eV)/kT)$  kHz ( the error of the pre-exponential factor is  $+1.1\times10^{10}$ ,  $-3.5\times10^{9}$ ). Thus the two remarkable features are consistently explained by the thermal jump and the dissociation within the  $(B_{s}$ - Si<sub>i</sub>) pair model.

The electric field gradient q at the  $B_{ns}$  site was precisely determined to be  $1.14 \pm 0.04 \times 10^{17} \text{ V/cm}^2$ . In order to make sure the atomic configuration for  $B_{ns}$  site, a theoretical calculation based on the KKR method for the energy minimum configuration and for the field gradient is urged.

It was disclosed that the broad resonance ( $\sim 10 \text{ kHz}$ ) from  $B_x$  site is due to static quadrupole interactions with no special symmetry. The fraction of  $B_x$  decreases as increasing temperature. From the these results, the most probable site for the  $B_x$  component is also the substitutional site with small electric field gradient due to crystal defects like vacancies. However, the detail of the character and the cause of this defect need further advanced investigation.

Although the present study is still in the first stage of the  $\beta$ -NMR study of semiconductor Si, we detected for the first time all the diamagnetic state of the implanted B and revealed a dynamic behavior of the boron related defects.

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#### Abstract

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# Acknowledgments

The author wishes to express his sincere gratitude to all of those who have helped to make this work successful:

Professor T. Minamisono for his proposing the present experiment, providing earnest guidance and discussing during the work, and encouragement. Associated Professor K. Matsuta for his providing earnest guidance and discussions, constant collaboration, and encouragement. Professor Y. Nojiri for his constant collaboration, discussions, and encouragement. Research Associate M. Fukuda for his constant collaboration, discussions, and encouragement.

Professor G. Langouche for his valuable advice and providing me with samples.

Dr. T. Ohtsubo for his constant collaboration, discussions, and encouragement.

Mr. Y. Takahashi for his technical supports during the experiment and for the Van de Graaff Accelerator.

Mr. M. Sakamoto for his technical supports during the experiment and for the developing the experimental setups.

Mr. T. Mizuta and Mr. K. Onishi for thier technical supports during the experiment.

Dr. M. Tanigaki, Mr. T. Miyake, and Dr. K. Sato for their collaboration and discussions during the experiment.

Dr. S. Momota, Dr. S. Fukuda, Dr. M. Mihara, Dr. T. Yamaguchi, Dr. K. Minamisono, and Ms. Y. Maruyama for their supports in the experiment.

Ms. K. Ohsawa for her technical support concerning paper works.

Last, but not least, I would like to thank Professor N. Takahashi, Professor T. Ohyama, Professor H. Akai, and Associated Professor T. Shimoda for their encouragement and for reading this thesis.

# Chapter 1 Introduction

We have investigated implantation sites of B and the related defects in semiconductor silicon by use of the  $\beta$ -NMR technique, which is one of the microscopic research methods. Because the implantation of boron as a dopant into semiconductor Si is quite useful technique for the fabrication of semiconductor devices, macroscopic phenomena, such as the range of ions, the distribution of damage and the annealing of damage have been well studied [Zie92, Mos80, K<sup>+</sup>86] in order to control the dopant location more strictly. However the microscopic knowledge like the implantation sites and the configuration and dynamics of defects has been still poor [FGP89].

Until now, ESR (Electron Spin Resonance) and channelling techniques have been widely used for the microscopic studies on the location of the boron in the lattice and on the defects associated with implantation. As described later, the ESR studies by Watkins on defects of electron-irradiated silicon greatly contributed to the physics of the defects in semiconductors [Wat63, Wat69, Sta98].

The NMR (Nuclear Magnetic Resonance) technique which is expected to bring the supplementary information of diamagnetic states of atoms is also quite helpful for the study of defects and lattice locations. It is, however, difficult to apply conventional NMR method to the dopants in semiconductors, because the NMR technique requires a large number of spins (typically  $10^{18}$  spins). Therefore there has been only a few NMR studies on boron in extremely highly doped silicon [SH64, HK91, H<sup>+</sup>92], which turns into, however, metallic Si whose electric properties are quite different from those of semiconductor Si.

In big contrast, the  $\beta$ -NMR technique used in the present study has great advantage compared with the conventional one, because of the large polarization of the probe nuclide, the short lived  $\beta$ -emitters, produced through nuclear reactions, that is a few hundred thousand times larger than the polarization created in nuclide placed in  $\sim 10$ kOe at thermal equilibrium at room temperature. Besides this advantage, because the measurement is based on the detection of the asymmetric  $\beta$ -ray distribution, this  $\beta$ -NMR has high sensitivity. For example, the impurity density of approximately  $10^8$ 

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spins/cm<sup>3</sup>·s was sufficient for the present study. Therefore, unlike the conventional NMR, the  $\beta$ -NMR technique is a very efficient tool for the study of dilute impurities such as dopants in semiconductor. In addition to this again, the high sensitivity of this technique makes the measurements free from the effect due to the radiation damages caused by its implantation. Such damages are unavoidable in the channelling experiments which required much more dose of ions into the sample.

Up to now, taking advantages mentioned above, the lattice location of <sup>12</sup>B in Si was already studied to some extent using the  $\beta$ -NMR technique by McDonald et al. [MM74, MM76], Minamisono et al. [MNDA83] and Ackermann et al. [MSS+90a, SFD+92] independently. From these researches, it was disclosed that a part of the implanted boron is settled at the substitutional site of Si lattice and its fraction relative to the all of the implanted B depends on the temperature. As temperature increases, the fraction of substitutional B increases. However, they gave different values on the fraction. This inconsistency has to be clarified. In addition to this discrepancy, a nonsubstitutional site with (111) axial symmetry was found by Ackermann et al. [FSD+92]. The fraction of the nonsubstitutional B has to be clarified since, it was not studied in detail then, at least on its temperature dependence etc.

Though the two implantation sites of B in Si were found by use of the ESR technique, the fractions of the discovered sites have been ambiguous still. In addition, the sum of borons in these two sites was considerably below the amount of the total implanted B. However, from the study of Minamisono et al. [MNDA83], it was known that the maintained polarization of <sup>12</sup>B is close to the reaction polarization at temperatures between 117 K and 285 K. In other words, there must be still missing fraction of B. In the present experiment, we studied all these two sites in detail as well as the identification of this missing fraction of B and their temperature dependences.

The followings are the contents of this paper. First of all overview of the previous studies on the lattice locations of B in Si will be described in the following section. In the next chapter, the principle of the  $\beta$ -NMR method used in this study will be described. In Chapter 3, the experimental apparatus, in Chapter 4, the experimental procedure and experimental results will be described. Finally in Chapter 5, interpretation of the present results will be given and will be compared with other previous studies.

# 1.1 Historical Overview

Before reviewing the microscopic studies like  $\beta$ -NMR, we will mention the annealing behavior of electrical activity of the B-implanted Si. The electrical activity is defined

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its implantation dose markedly.

In the present experiment, however, as the dose rate was about  $\sim 10^4 \text{ ions/cm}^2 \cdot \text{s}$ and the total dose for one run of the measurement was less than  $10^8$  ions/cm<sup>2</sup>, we can observe the phenomena arising from single B atom itself, free from the influence from other B impurities or the precipitated B cluster.

#### Channeling experiments

North and Gibson [NG70] and Fladda et al. [FBLS70] utilized  $\alpha$  particles emitted from the  ${}^{11}\mathrm{B}(p, \alpha)^8\mathrm{Be}$  reaction to investigate the lattice location of B atom in Si by use of the channeling technique. After implantation at room temperature the fraction of B in the substitutional site showed variety from about 60 % for a dose of  ${\sim}10^{14}~{\rm ions/cm^2}$ to about 30 % for a dose of  $\sim 10^{15}$  ions/cm<sup>2</sup>. They also found that the rest of the B atom does not occupy a perfect tetrahedral interstitial site, in contrast with the heavier group III elements [EDJM69]. For a reference, the naive pictures on the interstitial sites of B in the diamond structure is shown in Fig.1.4. In Fig.1.2, the experimental substitutional fraction given from the channeling experiments is illustrated as a function of dose (after Fink et. al [F+83]). As for a interstitial site, they suggested some kinds of configuration [F+83], but it could not be reliable to prove this due to the difficulty of the experiment or of the analysis of experimental results.

as the fraction of the electrical conductivity relative to that expected from the dopant density. So it shows the fraction of the effective dopants, hence, is a direct probe of the fraction of the B atom in the substitutional site. As shown in Fig.1.1, the annealing behavior depends on the dose rate. At low doses ( $< 10^{13}/cm^3$ ), the electrical activity increases as a function of temperature and approaches to 100 % monotonically, while at higher doses a 'negative annealing' region is observed. This negative annealing region II (in Fig.1.1) is interpreted in terms of a precipitation of B and formation of defects, where B atom is uncharged and cannot conduct carriers effectively. In region III, the number of substitutional B increases rapidly with the activation energy of about 5 eV. Since this activation energy is close to the sum of the formation energy of vacancy ( $\sim 4 \text{ eV}$ ) and the migration energy of the B atom ( $\sim 1 \text{ eV}$ ), this behavior in the region III is interpreted as the recombination of the precipitated B atom with the help of the vacancies which become thermally mobile. In this manner, the behavior of implanted atom depends on

#### ESR measurement

The defects in Si crystals were intensively studied by use of ESR and ENDOR (Electron Nuclear Double Resonance) techniques by Watkins *et al.* They have found B related defects in B-doped Si [Wat75, TW80]. The defects were introduced by the electron irradiation technique in Si samples at low temperature (20.4 K), and then observed photo induced ESR or ENDOR signals, which were stable up to 50 K. This phenomenon is interpreted as follows. The defect has two energy levels ( or three charge states of  $B^{(-)}$ ,  $B^{(0)}$  and  $B^{(+)}$ ) in the band gap of Si; a single donor level ( $B^{(0)}/B^{(+)}$ ,  $E_c = -0.13$  eV) and a single acceptor level ( $B^{(-)}/B^{(0)}$ ,  $E_c=-0.37$  eV) [TW80, HNW87] (Fig.1.3). This defect shows negative-U property [BKS80] due to the Jahn–Teller effect with the metastable state  $B^{(0)}$ . Among these charge state, only the  $B^{(0)}$  state is observed by ESR, because other two states are diamagnetic and are not detected. Initially, the  $B^{(-)}$  states are produced by the electron irradiation. By the photo transition the  $B^{(-)}$  states turn into the  $B^{(0)}$  states as follows and are detected by ESR,

$$\mathbf{B}^{(-)} \xrightarrow{h\nu} \mathbf{B}^{(0)} + e^{-}.$$

However, the  $B^{(0)}$  states release an electron to the conduction band by thermal activation at higher temperatures to be converted into  $B^{(+)}$  state as

$$B^{(0)} \xrightarrow{0.13 \text{ eV}} B^{(+)} + e^{-}.$$

As a result, ESR signal disappears at higher temperatures, since the ESR cannot detect the  $B^{(+)}$  state directly. Thus, warming the sample up to 50 K,  $B^{(0)}$  spectrum was lost, and, then by recooling it down to 20.4 K, the spectrum naturally appeared again.

The ESR study have established firmly that  $B^{(0)}$  state is in a low-symmetry site  $(C_{1h})$ , which distorted slightly from the position with axial  $\langle 111 \rangle$  symmetry  $(C_{3v})$  in the  $\{110\}$  plane. In the  $B^{(0)} \longleftrightarrow B^{(+)}$  thermal conversion, the major direction of  $\langle 111 \rangle$  axis of the defect is unchanged but the memory of the direction of the off-axis distortion is lost. From this fact, they suggested that  $B^{(+)}$  has pure  $\langle 111 \rangle$  axial symmetry and in the conversion to  $B^{(0)}$  it is distorted into one of the six possible directions provided by the three  $\{110\}$  planes containing this  $\langle 111 \rangle$  axis.

They also found that the major  $\langle 111 \rangle$  axis is changed to the other  $\langle 111 \rangle$  direction when warmed up to about 180 K with its activation energy of about 0.60 eV. Moreover, after warmed up to about 300 K, no spectrum was observed. This thermal activation energy was proven to be about 0.6 eV, which was same as the activation energy for the  $\langle 111 \rangle$  direction change. From this same activation energies of the direction change and

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the annealing, they concluded that a migration causes not only the changes of the major (111) axis but also the annealing of the defect.

As mentioned above, though Watkins *et al.* found this B-related defect in Si and measured various properties of it, its microscopic configuration is still unknown. They proposed three possible configurations which agree with the observed symmetry of the defect (Fig.1.5).

#### $\beta$ -NMR measurements

One of the sophisticated NMR method, the  $\beta$ -NMR, was developed at Osaka university by Sugimoto [S<sup>+</sup>66] and has been improved by Minamisono *et al.* [MNS74, M-NO81, M<sup>+</sup>92]. Although it was developed in order to study nuclear physics, especially to measure nuclear moments, it was revealed to be a unique tool to investigate ion implantation process and hyperfine fields in solids [HNN<sup>+</sup>76, MY81, Min85, ONM<sup>+</sup>93, MSA<sup>+</sup>98]. However, a very few  $\beta$ -NMR experiments on semiconductor were carried out, compared with the studies on metallic samples so far. In Table 1.1, the studies on the locations of impurities in semiconductor Si are listed.

1.1. HISTORICAL OVERVIEW

Method Temperature

 ${}^{10}B({}^{3}He,n){}^{12}N \beta$ -NMR 100-980K

 $E_i=3.0 MeV$   $\beta$ -asym Unspecified

Laser

separated beam

fragmentation of mass-

Dopant

30-300K

pumping Si, Si(B), Si(P)

(Cont.) Impurity

(Probe)

Nitrogen

 $\theta_R=20^\circ$ 

Litium <sup>8</sup>Li:

p-induced

Table 1.1  $\beta$ -NMR studies on locations of impurities in semiconductor Si.

Impurity	Method	Temperature	Results	Ref.
(Probe)		Dopant	Remarks	-
Boron				
${}^{11}B(d,p){}^{12}B$	$\beta$ -NMR	RT	$ u_L $	JILLING ST
$E_i = 1.5 MeV$		Unspecified (100-200	$\Rightarrow$ Frequency shifts	[MM74]
$\theta_R = 45^{\circ}$		$\Omega \mathrm{cm}$ )	(compared with metallic hosts)	
${}^{11}B(d,p){}^{12}B$	$\beta$ -NMR	RT	$\Delta \nu_L, \Delta a \text{ (around } \nu_L(\text{AFP}))$	
$E_i = 1.5 MeV$		Unspecified (130 $\Omega$ cm	$\Rightarrow f(\mathrm{sub}) = 67(6)\%$	[MM76]
$\theta_R = 45^{\circ}$		)	I he are an it is shown in the	
${}^{11}B(d,p){}^{12}B$	$\beta$ -NMR	100-900K	$\Delta a(T)$ around $\nu_L$ (+ - 10 kHz),	100-1-01
$E_i = 2.9 MeV$	$\beta$ -asym	Unspecified	$P(H_{ext})$	[MNDA83
$\theta_R=20^\circ$			$\Rightarrow f(sub(\nu_L \pm 10 kHz)) = 26 \sim$	
			92% (100~900K)	
			$P/P_0 = 100\% (117 \sim 285 \text{K})$	
${}^{11}B(d,p){}^{12}B$	$\beta$ -NMR	300~950K B (5×10 <sup>18</sup> ,	$\Delta a(T) \Rightarrow f(sub) = 20 \sim 100\%$	
$E_i = 1.5 MeV$		$2 \times 10^{15}, < \times 10^{13}$ /cc)	(300~950K)	[MSS <sup>+</sup> 90a
$\theta_R = 45^{\circ}$		P (< $\times 10^{13}$ , 9 $\times 10^{14}$	Annealing process	MSS <sup>+</sup> 90b
		/cc) Sb $(1.5 \times 10^{18}$ /cc)		
${}^{11}B(d,p){}^{12}B$	$\beta$ -NMR	320K, 280K	eqQ/h=360(15)kHz at 320K	
$E_i = 1.5 MeV$		B $2 \times 10^{15}/cc$	(111) B <sup>+</sup> .	[FSD+92]
$\theta_R = 45^{\circ}$			Jump between four $\langle 111 \rangle$ direc-	
			tions. Vanish $eqQ$ split at 280K.	
${}^{11}B(d,p){}^{12}B$	$\beta$ -NMR	50-1000K B $(5 \times 10^{18},$	$\Delta a(T),$	
$E_i = 1.5 MeV$		$2 \times 10^{15}, < \times 10^{13}$	eqQ split. $\Rightarrow f(sub)=0\sim100\%$	[SFD+92,
$\theta_R = 45^{\circ}$		/cc), P (< $\times 10^{13},$ 9 $\times$	(50~1000K).	FSF <sup>+</sup> 93]
		$10^{14}, 3 \times 10^{18} / \text{cc}),$	$\Rightarrow$ Annealing process	
		Sb $(1.5 \times 10^{18} / cc)$		
${}^{11}B(d,p){}^{12}B$	$\beta$ -NMR	240,340K	At 240K eqQ/h=375(15)kHz	
$E_i = 1.5 MeV$		$P(9 \times 10^{14} / cc)$	$\langle 111 \rangle \Rightarrow B^+$ charge state.	[FAD+93]
$\theta_R = 45^{\circ}$		The dasher to blank to	Disappear at 340K.	
${}^{11}B(d,p){}^{12}B$	β-NMR	$50K \sim 370K B (5 \times 10^{18},$	$\Delta a(T)$ at $\nu_Q$	
$E_i = 1.5 MeV$		$2 \times 10^{15}$ /cc), P (9 ×	$\Rightarrow$ Diffusive jumping.	[FDE+94]
$\theta_R = 45^{\circ}$		10 <sup>14</sup> , Schottoky diodes		
		(Au 50nm))		

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(Cont.)

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Results Remarks

.

Ref.

7

No NMR signal near  $\nu_L$ ,  $P/P_0=37\sim0\%(100\sim980\text{K})$ 

[MNDA83]

NMR at  $\nu_L$ ,  $\Delta \nu_L$ ,  $\Delta a(T)$ 

[B<sup>+</sup>88]

#### CHAPTER 1. INTRODUCTION

Using the advantage of  $\beta$ -NMR method for dilute impurity, the first  $\beta$ -NMR experiment on <sup>12</sup>B implanted in Si was performed by McDonald *et al.* [MM74, MM76]. They observed a sharp resonance at the Larmor frequency and measured the linewidth as a function of crystal orientation relative to the external magnetic field. Comparing the experimental linewidths with the theoretical values obtained from second-moment calculations of the dipolar broadening (Table 1.2), they concluded that the resonance came from the <sup>12</sup>B nuclei in the substitutional sites. They also deduced the fraction of substitutional B (67  $\pm$  7 %) at room temperature from the amplitude of the spectrum.

In 1983, the temperature dependence of the substitutional <sup>12</sup>B fraction was observed by Minamisono *et al.* for the first time [MNDA83]. As shown in Fig.1.6, the fraction is about 30 % at the low temperature (100 K) and it increases with temperature until it reaches 100 % at 800 K. It is noted that the fraction at temperatures between 300 K and 500 K shows constant plateau. On the contrary, they also revealed that all the polarization of <sup>12</sup>B produced in nuclear reaction is maintained below 285 K, though only a part of the polarization was observed at the Larmor frequency. Thus two problems have been left unsolved; why the substitutional fraction shows such temperature dependence and where is the location of the missing <sup>12</sup>B at low temperatures.

Crystal	Linewidth (FWHM in Hz)						
orientation	Exp.	Theory (substitutional)	Theory (Tetrahedral)				
$\langle 100 \rangle$	$107 \pm 19$	80	197				
$\langle 110 \rangle$	$168 \pm 19$	196	202				
(111)	$194 \pm 19$	220	203				

Table 1.2 Line widths of the resonances at the Larmor frequency. (From [MM76].)

Since 1990, a research group in Germany has been studying on this problem. Their results are summarized as follows ( [MSS<sup>+</sup>90a, SFD<sup>+</sup>92, FSF<sup>+</sup>93, FSD<sup>+</sup>92, FDE<sup>+</sup>94]).

(1) As shown in Fig.1.7, the fraction of the substitutional B is almost zero at low temperature (50 K). It increases monotonically to almost 100 % at high temperature.

(2) The fraction of the substitutional B depend not only on temperature but also on the type and the density of the dopant. In the heavily p-type impurity doped Si case, a plateau was found at above 400 K. Going toward intrinsic material and toward further n-type impurity doped material the plateau becomes shorter and eventually disappears completely. Another remarkable feature is the doping dependence of the saturation

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temperature. It increases from 600 K to 1000 K going from heavily doped n-type Si to heavily doped p-type Si.

(3) According to their qualitative interpretation, there are two sites for the implanted  $^{12}$ B, one is substitutional site and the other is nonsubstitutional site; primary location just after the implantation is the nonsubstitutional site independent of temperature, and then nonsubstitutional B diffuse into the substitutional site by thermal activation within the nuclear lifetime of  $^{12}$ B. Based on this view, they deduced activation energies as shown in Table 1.3.

Table 1.3 Activation energy for a substitutional B in Si. (After [MSS+90a])

			Dopant		Logarithm of pre-exponent	Activation energy
Sample	Type of	Deret	concentration	Production	factor	$E_a$
number	conduction	Dopant	(cm °)	process	$\log_{10}(\mu_0 [HZ])$	(ev)
1	р	В	$5 \times 10^{18}$	CG	$7.3^{+4.2}_{-2.8}$	$0.9^{+0.6}_{-0.4}$
2	р	В	$2 \times 10^{15}$	CG	$5.3^{+2.6}_{-1.7}$	$0.5^{+0.3}_{-0.2}$
3	р	В	$\leq 10^{13}$	FZ	$5.6^{+3.5}_{-2.0}$	$0.5^{+0.4}_{-0.2}$
4	n	Р	$\leq 10^{13}$	FZ	$6.5^{+5.5}_{-2.5}$	$0.6^{+0.6}_{-0.3}$
5	n	Р	$9 \times 10^{14}$	FZ	$3.3^{+1.5}_{-2.3}$	$0.23 \pm 0.15$
6	n	Sb	$1.5  imes 10^{18}$	CG	$4.1 \pm 1.8$	$0.23 \pm 0.15$

(4) From these results, they suggested that the nonsubstitutional B is identified with the defect of the  $B^{(+)}$  which was found previously by ESR study, because the deduced activation energy of the nonsubstitutional B agrees with that of the  $B^{(+)}$  found by ESR for the same doping level.

(5) They found quadrupole split resonance in the NMR spectra for p-type Si at 320 K. It shows  $\langle 111 \rangle$  axial symmetry with the coupling constant |eqQ/h| of 360 kHz. They demonstrated that the <sup>12</sup>B in this site thermally migrate between the four identical sites which correspond to the four  $\langle 111 \rangle$  axis of the crystal. This fact also agrees with the case of the B<sup>(+)</sup> found by ESR which was supposed to be  $\langle 111 \rangle$  axial symmetry and shows the same thermal behavior.

(6) The fraction of  ${}^{12}B$  in this site with quadrupole split also depends on the temperature. The resonance disappears as temperature increases. The temperature dependence

8

CG=Crucible Grown, FZ=Float Zone

slightly depends on the type and the density of dopants. For a heavily doped p-type Si, the resonance remains up until higher temperature than for the n-type Si (Fig.1.8). They performed the same measurement using the Schottky diode made of n-type Si, in order to observe the effect of the Fermi level. When a reverse bias was applied to it at T = 340 K so as to move the Fermi level, the quadrupole split resonance, which was not observed in the n-type Si was observed. However, the details are not clarified yet.

As described above, the location of the implanted B is still ambiguous except for the substitutional site. Besides, even among  $\beta$ -NMR studies the fraction of the substitutional sites at room temperature are inconsistent with each measurement (Table 1.4).

As previously stated, the purpose of this study is to confirm the fractions of the B located in each site definitely as a function of temperature, and the property and behavior of the B atom in the  $\langle 111 \rangle$  axial-symmetry site, which cannot be clarified by the ESR method.

Table 1.4 The fractions of the substitutional B implanted into Si at room temperature  $(\sim 300 \text{ K})$ .

Method	Substitutional fraction (%)	Dopant	Dose	Reference
Channeling	63	1-100 Ω cm n-, & p- type	$1.1 \times 10^{14} \ /\mathrm{cm}^2$	[FBLS70]
$\beta$ -NMR	$67\pm 6$	$130 \ \Omega \ \mathrm{cm}$	$10 \times 10^{10} \ /\mathrm{cm}^2$	[MM76]
$\beta$ -NMR	~50		$< 10 \times 10^5 \ /\mathrm{cm}^2 \ /\mathrm{s}$	[MNDA83]
$\beta$ -NMR	$20 \sim 30$	various	$< 10 \times 10^5 \ /\mathrm{cm}^2 \ /\mathrm{s}$	[MSS <sup>+</sup> 90a]

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1.1. HISTORICAL OVERVIEW



Figure 1.1 Effect of dose on the electrical activity to prove the fraction of ion implanted boron in substitutional site during annealing  $T_A$ . (after [NG71])

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CHAPTER 1. INTRODUCTION





Figure 1.2 The substitutional fraction of boron in silicon in the region of maximum concentration as a function of implantation dose and annealing temperature. • · · · [AH73], × · · · [SJF78], • · · · [SB73],  $\triangle \cdot \cdot \cdot$  [F-BLS70],  $\Box \cdots$  [NG70]. The numbers at each point indicates the measured substitutional fractions, corresponding to the maximum of the implanted B concentration profiles. Contour lines are drawn to guide the eye. (after [F+83]).

Donor

0.13 eV

[HNW87])



Tetrahedral site

.

Accepter 0.37 eV

Ev

Figure 1.3 Electrical level structure for interstitial boron in silicon observed by ESR and DLTS (Deep Level Transient Spectroscopy). (after



Hexahedral site

Figure 1.4 Three naive pictures on the possible interstitial sites of B implanted in diamond lattice. All these three sites have high symmetry. However, as for B atom in Si, neither by the channeling nor by the ESR study they could observe the B atom at these sites.



Figure 1.5 Models for the location of B in Si. (a) a bent-bond-centered Si – B - Si interstitialcy; (b) a bent-bond Si - Si - B configuration, which can be viewed as a distortion from tetrahedral interstitial site; (c) a distortion from the the hexagonal interstitial site. (after [Wat75])

. . . .



(after [MNDA83])

Figure 1.6 Polarization observed at  $\nu_L$  vs. temperature for <sup>12</sup>B in Si and Ge. The rf was modulated by 20 kHz at  $H_{\text{ext}} = 5.0$  kOe. The dashed line indicates the full polarization of  $^{12}B$  produced in the reaction.







[001])=6.5°. (after [FDE+94])



Figure 1.8  $\beta$ -NMR signal intensities of the quadrupole shifted resonance  $I(\nu_{Q1})$  corresponding to  $B_i^+$  as function of temperature for three differently doped samples: no.1: Si:B ( $c=5 \times 10^{18} / cm^3$ ), no.2: Si:B  $(c=2 \times 10^{15} / cm^3)$ , no.5: Si:P  $(c=9 \times 10^{14} / cm^3)$ . The inset shows a  $\beta$ -NMR spectrum for sample no.5 at T=240 K, B=400.6 mT,  $\angle$ (B,

# Chapter 2 Experimental methods

Due to the parity violation in weak interactions, the angular distribution of  $\beta$  rays from  $\beta$  emitting nuclei is asymmetric with respect to the nuclear spin I. So the distribution of the  $\beta$  ray is a good probe to detect nuclear spin polarization:  $\beta$ -NMR is the advanced NMR technique in which the asymmetric emission of  $\beta$  rays is detected [Con59, S<sup>+</sup>66]. Fundamental concepts of NMR will be mentioned in Appendix A.

The  $\beta$ -NMR technique has been used not only for the measurement of nuclear moments of  $\beta$  emitting nuclei but also for the studies of solid-state physics. The wide applicability of the  $\beta$ -NMR technique is basically because of the following special features of the technique.

- Large NMR effects, *i.e.*, high sensitivity even for very dilute impurities implanted in various materials.
- Wide variety of combinations of host and impurity atoms.
- High precision in determining the local fields in a crystal lattice.
- Simplicity in measuring spin relaxation phenomena in the time range of the nuclear lifetime.

Because of its high sensitivity (typically below  $10^9$  nuclei are sufficient), this method has an advantage in investigating the hyperfine interactions of very dilute impurities like a dopant in semiconductors.

The technique consists of the following 4 procedures:

- (1) Production of the polarized  $\beta$ -emitting nuclei through nuclear reaction.
- (2) Implantation of the  $\beta$  emitters into materials to preserve polarization produced in the reaction.
- (3) Detection of the polarization by means of  $\beta$ -ray asymmetry.
- (4) Resonant destruction or inversion of the spin polarization by NMR.

In this chapter, principle of the  $\beta$ -NMR technique are described. Experimental apparatus and setup, including sample treatment will be described in the next chapter.

2.1.  $\beta$ -NMR TECHNIQUE

#### $\beta$ -NMR technique 2.1

## 2.1.1 Production of polarized nuclei

the polarization parallel to  $k_i \times k_f$  is defined to be positive in this issue.

We chose the recoil angle of  $40^{\circ} \pm 2.5^{\circ}$  and incident deuteron energy of 1.5 MeV. to optimized the polarization and production rate of  ${}^{12}B$  nuclei [T+76]. In this condition typical polarization is approximately 11 %.

### 2.1.2 Preservation of nuclear polarization

The recoil products are implanted into a catcher sample by use of the its recoil energy obtained in the nuclear reactions. Because of the target thickness, recoil energy of the out-going nuclei are distributed from 0 to maximum energy due to the finite target thickness which degrade the out-going energy. Because of the energy distribution, the charge state also distributes widely. If the nuclear spin I and the atomic spin J are not decoupled, the nuclear spin is disturbed by the atomic spin through the strong hyperfine interactions between the spins resulting in the destruction of the nuclear polarization produced in the reaction. To decouple the interaction between the nuclear spin and the atomic spin during flight in vacuum, a strong magnetic field was applied in the region from the reaction target to the implantation medium.

### 2.1.3 Detection of polarization

The polarization of the  $\beta$  emitters are observed from asymmetric distribution of  $\beta$ rays. The angular distribution of  $\beta$  rays from polarized  $\beta$  emitters is given as

$$W(\theta) =$$

where  $\theta$  is the polar angle of the electron momentum relative to the polarization axis, vis the velocity of the electron, c is the light velocity, A is the asymmetry parameter of the  $\beta$  decay, and P is the polarization of  $\beta$  emitting nuclei.

In the present experiment, hyperfine interactions of <sup>12</sup>B implanted Si crystal have been studied. <sup>12</sup>B nuclei are produced through <sup>11</sup>B(d,p)<sup>12</sup>B reaction (Q = 1.149 MeV). A large polarization is obtained in the product nuclei by selecting recoil angle and incident beam energy  $[T^+76]$ . The direction of the polarization is perpendicular to the reaction plane defined by the incident beam momentum  $k_i$  and the recoil beam momentum  $k_f$ ;

$$1 + \frac{v}{2}AP\cos(\theta),\tag{2.1}$$

### CHAPTER 2. EXPERIMENTAL METHODS

In the present case (  ${}^{12}B(1^+) \rightarrow {}^{12}C(0^+)$  ),  $v/c \approx 1$ , and A = -1, so the equation 2.1 can be simply written as

$$W(\theta) = 1 - P\cos(\theta). \tag{2.2}$$

For an efficient measurement of the spin polarization,  $\beta$ -ray counters were placed at  $\theta = 0^{\circ}$  (up counter) and  $\theta = 180^{\circ}$  (down counter). The ratio  $R_{\text{off}}$  between the counting rate of the up counter  $(N_u)$  and that of the down counter  $(N_d)$  is thus given as

$$R_{\text{off}} = \frac{N_u}{N_d} = \frac{nG_u W(0^\circ)}{nG_d W(180^\circ)}$$
  
=  $\frac{G_u (1-P)}{G_d (1+P)},$  (2.3)

where n is the  $\beta$ -decay rate and  $G_u$  and  $G_d$  are the geometrical efficiencies for the up and down counters, respectively.

### 2.1.4 NMR detection

When an rf magnetic field is applied to the sample perpendicular to the external magnetic field, the polarization is changed diminished to  $P - \Delta P$  depending on the rf frequency  $\nu$  and intensity  $H_1$ . The ratio of the count rates then becomes

$$R(\nu, H_1) = \frac{G_u[1 - (P - \Delta P(\nu, H_1))]}{G_d[1 + (P - \Delta P(\nu, H_1))]}.$$
(2.4)

Normalized by the ratio  $R_{off}$ , the geometrical asymmetries are canceled out, and when  $P(P - \Delta P) \ll 1$ , the polarization change  $\Delta P(\nu, H_1)$  is deduced as

$$\Delta P(\nu, H_1) = \frac{[R(\nu, H_1)/R_{\text{off}}] - 1}{[R(\nu, H_1)/R_{\text{off}}] + 1}$$
(2.5)

#### Time sequence of $\beta$ NMR detection

In the present experiment, the pulsed beam method (next section) was employed to separate the counting period from the beam-on period to reject unwanted background. The rf was applied right after the beam-on period. Typical timing program was as shown in Fig.2.1 with schematics to explain  $\beta$ -ray yield and the nuclear spin polarization.

The time development of the polarization P(t) and the number of nuclei N(t) should hold the following differential equations;

$$\frac{d}{dt}P(t) = \frac{q}{N(t)}P_0 - (\Lambda + \lambda + W)P(t), \qquad (2.6)$$

$$\frac{d}{dt}N(t) = q - \lambda N(t).$$
(2.7)

#### 2.2. β-NQR METHOD

Here, the meaning of the parameters are as follows.

- $P_0$ : Initial polarization

The transition probability W for I = 1 nucleus is

$$W = \frac{1}{2} (\gamma H_1)^2 f(\nu), \quad \text{for sir}$$

where  $f(\nu)$  is the intrinsic line shape function.

Under the timing program shown in Fig.2.1, the polarization in the counting time is given as a function of time as

$$P(t) = P_0 \frac{\lambda}{\Lambda + \lambda + \lambda}$$

where  $t_1$  and  $t_2$  are the beam bombarding time and the rf time, respectively.

#### $\beta$ -NQR method 2.2

a modified  $\beta$ -NMR method, so called  $\beta$ -NQR method [M<sup>+</sup>92].

When the electric quadrupole interaction is much smaller than the magnetic interaction, it can be treated as a perturbation. In the first- and second-order perturbation theory, the transition frequency between substate m and m-1 is given (Appendix A) as

$$\nu_m = \frac{E_{m-1} - E_m}{h} = \nu_L + \nu_m^{(1)} + \nu_m^{(2)} + \cdot \quad (m = I, I - 1 \dots I + 1),$$
(2.10)  
$$\nu_m^{(1)} = -\frac{1}{2}\nu_Q(m - \frac{1}{2})(3\cos^2\theta - 1 + \eta\cos 2\phi\sin^2\theta),$$
(2.11)

For the given Larmor frequency  $\nu_L$ , the crystal orientation  $\theta$ ,  $\phi$  and the asymmetry parameter of the field gradient  $\eta$ , a set of transition frequencies can be calculated. In the

q: Implantation (production) rate of the nuclei (q = 0, except for beam-on period) A: Spin-lattice relaxation rate: reciprocal of the spin-lattice relaxation time  $T_1$  $\lambda$ : Decay-rate: reciprocal of the mean life of the nucleus  $\tau_{\beta}$  (29.1ms: for <sup>12</sup>B) W: Transition probability between magnetic substates by the destructive rf field.

ngle quantum transition  $\Delta m_I = \pm 1$ , (2.8)

 $\frac{1 - \mathrm{e}^{-(\Lambda + \lambda + W)t_1}}{1 - \mathrm{e}^{-\lambda t_1}} \mathrm{e}^{-\Lambda(t_2 + t)},$ (2.9)

If the nuclear quadrupole moment Q of a nucleus  $(I \ge 1)$  is not zero, the host atoms interact with electric field gradient q from the surrounding host atoms (Appendix A). Under the electric quadrupole interaction added to the magnetic interaction, the resonance frequency shifts from the Larmor frequency  $\nu_L$ , and the resonance line splits into 2I resonance frequencies. Because only a pair of neighboring sublevels is involved in a single transition, the NMR signal becomes weaker than the case of pure magnetic interaction (Fig.2.2). To observe NMR in good efficiency even in this case, we employed

present  $\beta$ -NQR method, simultaneous application of 2*I*-rf's corresponding to the correct coupling frequencies given above induce all the transitions and destroys polarization completely, as a schematically shown in Fig.2.3, in the case of  ${}^{12}B(I=1)$ .

Considering pure polarization, that is, initial substate populations are distributed linearly  $(a_m = \alpha m + \beta)$  and each transition is saturated by rf's, we will obtain full polarization, *i.e.*,  $P_0 = \alpha (I+1)(2I+1)/3$ . On the other hand, in conventional  $\beta$  NMR, *i.e.* when a pair of substate populations are equalized, the obtained polarization change is reduced to  $\alpha/2$ . So that, 2(I+1)(2I+1)/3 times larger polarization change is expected by the present  $\beta$ -NQR method. Thus, this technique help NMR measurement effective especially for large spin I. For the nuclei with I = 1 like <sup>12</sup>B the enhancement factor is already 4. This means  $32 (= 4^2 \times (2I))$  times more effective than the conventional NMR.

#### 2.3 Relaxation mechanisms of nuclear polarization

### 2.3.1 General

The nuclear polarization produced through nuclear reaction decreases as a function of time toward the value in the thermal equilibrium which is practically zero compared with the preset nuclear polarization. The motion of the polarization is described phenomenologically by the Bloch equations using the spin-lattice relaxation time  $T_1$  and the spin-spin relaxation time  $T_2$  as

$$\frac{d\langle I_z\rangle}{dt} = -\frac{\langle I_z\rangle - I_{z0}}{T_1},$$
(2.12)

$$\frac{d\langle I_x\rangle}{dt} = \gamma \left(\langle I \rangle \times H\right)_x - \frac{\langle I_x \rangle}{T_2}, \qquad (2.13)$$

$$\frac{d\langle I_y\rangle}{dt} = \gamma \left(\langle I \rangle \times H\right)_y - \frac{\langle I_y \rangle}{T_2}.$$
(2.14)

 $T_1$  represents the rate of the relaxation of the polarization  $\langle I_z \rangle$  toward the thermal equilibrium value  $I_{z0}$ , caused by contact with the lattice as a thermal reservoir.  $T_2$  is the characteristic time for the dephasing process of the spin ensemble.

Here, we concentrate on  $T_1$ . There are two essential causes for the relaxation. One is due to a fluctuating local fields at the nucleus, and the other is due to spin-flip scattering with electrons known as the Fermi contact interaction. In order to explain the experimental results quantitatively, we will describe these relaxation mechanism in this section.

#### 2.3. Relaxation mechanisms of nuclear polarization

#### Spin-lattice relaxation by the motion of the atom 2.3.2

A nucleus in matter interacts with the internal local fields, such as the magnetic field and the electric field gradient, produced by the neighboring atoms as well as with the external fields. The local field varies according to the lattice site of the atom, because the local field depends on the geometrical configuration around the nucleus. Therefore, when the atom jumps from a lattice site to the other, the nucleus experiences a timevarying local field. It can cause the polarization relaxation. The mean residence time  $\bar{\tau}$ of an atom, which is an average of the time bin that an atom stays at a lattice site, can be described by the Arrhenius formula,

$$\frac{1}{\bar{\tau}} = \frac{1}{\tau_0}$$

$$P(\tau) =$$

Therefore, the distribution of the jump frequency is obtained by Fourier transformation of  $P(\tau)$ 

$$(\omega) = \frac{1}{2}$$
$$= \frac{2}{2}$$

$$\frac{1}{T_1}$$
 o

The characteristic time for the changes of the local field is, in fact, the correlation time  $\tau_c$  of the Hamiltonian of a system, which tells how long the Hamiltonian at a certain moment is correlated to a later value, which is, within a factor of order unity, the same as the mean residence time  $\bar{\tau}$  described above. Fig.2.5 shows the relaxation rate  $1/T_1$  as a function of the correlation time. According to eq.(2.18), it is shown that for  $\tau_c \ll 1/\omega_L$ , the  $1/T_1$  is proportional to  $\tau_c$ ; for  $\tau_c \gg 1/\omega_L$ ,  $1/T_1$  is proportional to  $1/\tau_c$ . That is, the relaxation rate  $1/T_1$  is strongest at  $\tau_c = 1/\omega_L$ . Therefore, under assumption of the Arrhenius behavior, the relaxation time becomes shorter as increasing temperature till it

$$\exp\left(-\frac{E_a}{kT}\right),\tag{2.15}$$

where  $\tau_0$  is the mean residence time at infinite temperature,  $E_a$  is the activation energy for a jump. Each jump usually obeys the Poisson process with the mean occurrence of  $1/\bar{\tau}$ , and then the distribution of the residence time  $\tau$  is expressed by a simple exponential

$$P_0 \exp\left(-\frac{|\tau|}{\overline{\tau}}\right). \tag{2.16}$$

$$\frac{1}{\pi} \int_{-\infty}^{\infty} P(\tau) e^{-i\omega\tau} d\tau$$

$$\frac{P_0}{\pi} \frac{\bar{\tau}}{1+\omega^2 \bar{\tau}^2}.$$
(2.17)

As shown in Fig.2.4, when the frequency distribution has a component at the Larmor frequency  $\omega_L$  (for the case of spin I = 1/2), it causes the polarization relaxation. Thus, the quantity  $P(\omega_L)$  is proportional to the transition rate and hence the relaxation rate

$$\leq \frac{\overline{\tau}}{1+\omega_L^2 \overline{\tau}^2}.$$
 (2.18)

reaches minimum at a certain temperature, and then becomes longer as the temperature. Thus, the relaxation time can be seriously short only in a certain temperature range.

Now a quantitative formula will be given to the above described qualitative discussion on the relaxation of the nuclear polarization (mainly following after Ref. [Abr63, Sli90]). This will be important formula for the later analysis. Since the nuclear polarization is a statistical physical quantity of spin ensemble, the motion of polarization is described using a density matrix  $\rho$  of the system in the quantum mechanics treatment. The statistical average  $\langle Q \rangle$  of any observable Q can is expressed as follows, when the density matrix of the spin system is given.

$$\langle Q \rangle = \operatorname{Tr} \{ \rho Q \} \,. \tag{2.19}$$

So, the motion of  $\langle Q \rangle$  can be described as

$$\frac{\mathrm{d}}{\mathrm{d}t} \left\langle Q \right\rangle = Tr \left\{ \left( \frac{\mathrm{d}\rho}{\mathrm{d}t} \right) \cdot Q \right\}.$$
(2.20)

Therefore, we know the motion of  $\langle Q \rangle$  by solving the equation of motion for the density matrix  $\rho$ ,

$$\frac{1}{i}\frac{\mathrm{d}\rho}{\mathrm{d}t} = -\left[\mathrm{H},\rho\right].\tag{2.21}$$

When the Hamiltonian is separated into two parts, *i.e.*,  $H(t) = H_0 + H_1(t)$ , the sum of a large static component  $H_0$  and a small time-dependent component  $H_1$ , where the  $H_0$ commutates with Q, the equation of motion can be written in the interaction representation as

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle Q \rangle = \mathrm{Tr} \left\{ \left( \frac{\mathrm{d}\rho^*}{\mathrm{d}t} \right) \cdot Q \right\}, \qquad (2.22)$$

$$\frac{1}{i}\frac{d\rho^*}{dt} = -[H_1^*(t), \rho^*], \qquad (2.23)$$

where  $H_1^*(t)$  and  $\rho^*(t)$  are defined by,

$$H_1^*(t) = \exp(iH_0t/\hbar)H_1\exp(-iH_0t/\hbar),$$
 (2.24)

$$\rho^*(t) = \exp(iH_0 t/\hbar)\rho \exp(-iH_0 t/\hbar). \qquad (2.25)$$

Integrating eq.2.23 from -t to t and making successive approximation to the second order of  $H_1$ , we obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho^{*}(t) = -\frac{1}{2\hbar^{2}}\int_{-t}^{t}\mathrm{d}\tau \left[\mathrm{H}_{1}^{*}(0), \left[\mathrm{H}_{1}^{*}(\tau), \rho^{*}(t)\right]\right].$$
(2.26)

#### 2.3. RELAXATION MECHANISMS OF NUCLEAR POLARIZATION

Since there are numbers of ensembles of systems of identical  $H_0$  and  $\rho$ , the average of these ensembles should be treated as

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho^*(t) = -\frac{1}{2\hbar^2}$$

product of the spin component  $A_a$  and the space-time component  $F_a$  as

$$H_1(t)$$

then the equation of motion is given as

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho^{*}(t) = -\frac{1}{2\hbar^{2}}\sum_{q,q'}\mathrm{e}^{i\left(\omega_{q}+\omega_{q'}\right)t}\int_{-t}^{t}\overline{G_{q'q}(\tau)}\mathrm{e}^{i\omega_{q}\tau}\mathrm{d}\tau \left[A_{q'},\left[A_{q},\rho^{*}\right]\right], \quad (2.29)$$

$$\overline{G_{q'q}(\tau)} = \overline{F_{q'}(0)F_{q}(\tau)},$$

$$\mathrm{H}_{0}A_{q} = \hbar\omega_{q}A_{q}.$$

is  $\overline{G_{q'q}(\tau)} = \delta_{-q'q} \overline{G_q(\tau)}$ , the equation 2.29 can be written as

$$\frac{d}{dt}\rho^*(t) = -\frac{1}{2\hbar^2}\sum_q \int_{-}^{t}$$

Thus, by substituting (2.30) into (2.22) the equation of motion of  $\langle I_z \rangle$  is obtained as

$$\frac{\mathrm{d}\langle I_z\rangle}{\mathrm{d}t} = -\frac{1}{2\hbar^2} \sum_q \int_{-\infty}^{\infty} G_q(\tau) \mathrm{e}^{-i\omega_q \tau} d\tau \operatorname{Tr}\left\{ \left[ A_{-q}, \left[ A_q, \rho^* \right] \right] \right\} \langle I_z \rangle , \qquad (2.31)$$

where the limit of integration is taken to be  $\pm \infty$ , so that it becomes independent of time as is in the case with  $t \gg \tau_c$ .

From the equation (2.31), if the correlation function  $G(\tau)$  of the spin system is given, the relaxation time can be calculated. The explicit form of the correlation function depends on the detail process of the atomic jump.

#### Polarization relaxation due to the fluctuation of the 2.3.3electric field gradient

In this section, using the equation (2.31) the relaxation time due to the fluctuation of the local electric field gradient will be given for the analysis of the present experimental results.

$$\overline{\mathrm{d}\tau \left[\mathrm{H}_{1}^{*}(0), \left[\mathrm{H}_{1}^{*}(\tau), \rho^{*}(t)\right]\right]}.$$
(2.27)

For the spin polarization,  $Q=I_z$ , when the perturbation Hamiltonian is given by the

$$=\sum_{q}A_{q}F_{q}(t),$$
(2.28)

Assuming that the correlation of each component suffixed by q is independent, that

$$G_q(\tau)e^{-i\omega_q\tau}d\tau \left[A_{-q}, [A_q, \rho^*]\right].$$
 (2.30)

#### CHAPTER 2. EXPERIMENTAL METHODS

Suppose the case that only the direction of the principal axis of the electric field gradient around a nucleus changes with time, with its coupling constant unchanged. The perturbation Hamiltonian is written as

$$H_1 = H_Q = \frac{eqQ}{4I(2I-1)} \sum_q F^q(t) A^q, \qquad (2.32)$$

$$F^{q}(t) = \begin{cases} \sqrt{\frac{4\pi}{5}} Y_{2}^{0}(\Omega(t)) & \text{for } q = 0\\ \sqrt{\frac{6\pi}{5}} Y_{2}^{-1}(\Omega(t)) & \text{for } q = 1\\ -\sqrt{\frac{6\pi}{5}} Y_{2}^{1}(\Omega(t)) & \text{for } q = -1 \\ \sqrt{\frac{6\pi}{5}} Y_{2}^{-2}(\Omega(t)) & \text{for } q = 2\\ \sqrt{\frac{6\pi}{5}} Y_{2}^{2}(\Omega(t)) & \text{for } q = -2 \end{cases}$$
(2.33)

$$A^{q} = \begin{cases} 3I_{z}^{2} - I^{2} & \text{for } q = 0\\ I_{+}I_{z} + I_{z}I_{+} & \text{for } q = 1\\ I_{-}I_{z} + I_{z}I_{-} & \text{for } q = -1\\ I_{+}^{2} & \text{for } q = 2\\ I_{-}^{2} & \text{for } q = -2 \end{cases}$$
(2.34)

where  $Y_2^q$  is the second-order spherical harmonics and the direction of the electric field gradient is denoted by  $\Omega$ . Using eq.(2.31) we obtain

$$\frac{\mathrm{d}\langle I_z\rangle}{\mathrm{d}t} = -\frac{1}{2\hbar^2} \left\{ \frac{eqQ}{4I(2I-1)} \right\}^2 \sum_q k_q(\omega_q) \mathrm{Tr}\left\{ \left[ A^q, \left[ A^{-q}, I_z \right] \right] \rho^* \right\} \langle I_z \rangle,$$
(2.35)

$$k_q(\omega_q) = \int_{-\infty}^{\infty} \overline{F^{-q}(\Omega(0)) F^q(\Omega(\tau))} e^{-i\omega_q \tau} dt.$$
(2.36)

For the nuclei of spin I = 1 as is in the case of <sup>12</sup>B, the eq.(2.35, 2.36) can be simplified as

$$\frac{1}{T_1} = \frac{1}{\langle I_z \rangle} \frac{\mathrm{d}\langle I_z \rangle}{\mathrm{d}t} = \frac{(eqQ)^2}{8\hbar} \left\{ k_1(\omega_0) + 4k_2(2\omega_0) \right\}.$$
(2.37)

As mentioned above, the correlation function depends on a specific model of the fluctuation such as the path and frequency of the atomic jump. For example, the expression of relaxation mechanism due to fluctuation of the electric field gradient which shows entirely isotropic change such as the rotation of a molecule has been widely used in the analysis of behavior of the atoms and molecules.

#### 2.3. RELAXATION MECHANISMS OF NUCLEAR POLARIZATION

 $\tau_c$ .) In this case, the correlation function between t = 0 and  $t = \tau$  is given as

$$\overline{F^q(0)F^q(\tau)} = \frac{\alpha}{4} \left\{ P_A(\tau) \sum_i \mathbf{Y}_2^q(\Omega_i) \mathbf{Y}_2^q(\Omega_i) + P_B(\tau) \sum_{i \neq j} \mathbf{Y}_2^q(\Omega_i) \mathbf{Y}_2^q(\Omega_j) \right\},\tag{2.38}$$

where  $\Omega_i$  (i=1, 2, 3, 4) are the directions of the field gradients,  $P_A(\tau)$ ,  $P_B(\tau)$  are the probabilities for an atom to be found in the same site or in the different sites after  $t = \tau$ , respectively.  $\alpha$  is  $4\pi/5$  for q=0 and  $6\pi/5$  for q=1, 2. When the rate of the jump is  $1/\tau_c$ , the  $P_A(\tau)$ ,  $P_B(\tau)$  can be calculated as

Then we obtain the correlation functions as

$$k_1(\omega_0) = \frac{1}{4} \frac{2\tau}{1 + \omega_0^2 \tau_c^2},\tag{2.41}$$

$$k_2(2\omega_0) = \frac{5}{16} \frac{2\tau}{1+4\omega_0^2 \tau_c^2}.$$
(2.42)

Detail of these calculations will be described in Appendix C. In conclusion, the relaxation time for this jump model is given by the equations (2.37), (2.41), and (2.42)

#### 2.3.4Spin-lattice relaxation due to conduction electrons

There is another important spin-lattice relaxation process due to conduction electrons. It can be explained as spin between of the nuclear spin I and the spins of conduction electrons. This process is a dominant mechanism of the relaxation in metals not in semiconductors. So, only a brief summary will be given here.

The Fermi contact interaction is proportional to the square of the electron wave function at the nucleus  $|\phi(0)|^2$ . Then transition probability is obtained as

$$\frac{1}{T_1} = \frac{(4\pi)^3}{9} \gamma_n^2 \gamma_n^2$$

where  $D(E_F)$  is the density of state at the Fermi surface.

Here, we assume the following model in order to deduce the correlation functions  $k_1$ and  $k_2$ . There are four electric field gradients which are different in its directions but identical in strength. The atoms are jumping from a site to another site with the mean jumping rate  $1/\tau_c$ . (The time required for a jump is assumed to be much shorter than

$$A_{4}(\tau) = \frac{1}{4} + \frac{3}{4}e^{-4\tau/3\tau_{c}}$$

$$B_{3}(\tau) = \frac{1}{4} - \frac{1}{4}e^{-4\tau/3\tau_{c}}$$

$$P_{4}(\tau) + 3P_{B}(\tau) = 1$$

$$(2.39)$$

$$(2.40)$$

$$\hbar^3 |\phi(0)|^4 D(E_F)^2 k_B T, \qquad (2.43)$$

### CHAPTER 2. EXPERIMENTAL METHODS

Since the frequency shift K (the Knight shift) in a magnetic field due to the paramagnetism of the conduction electrons for Fermi gas is also proportional to  $|\phi(0)|^2 D(E_F)$ , that is

$$K \equiv \frac{\Delta H}{H} = \frac{4\pi}{3} \gamma_e^2 \hbar^2 |\phi(0)|^2 D(E_F), \qquad (2.44)$$

so the relaxation time and the Knight shift have the relation known as the Korringa relation,

$$K^2 T_1 T = \frac{\hbar}{4\pi k_B} \left(\frac{\gamma_e}{\gamma_n}\right)^2. \tag{2.45}$$

Although this formula gives only a contribution from the s-state electron, it is still useful to predict spin-lattice relaxation time.

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Figure 2.1 Typical timing program for the  $\beta$ -NMR detection.







Initial polarization  $P_0$  $P_0 = \sum a_i m_i$ 

After applying rf

1) Conventional  $\beta$ -NMR method



#### 2) β-NQR method Simultanious application of rfs







Figure 2.3 Principle of the  $\beta$ -NQR method. The spectrum is measured as a function of the quadrupole coupling constant.



CHAPTER 2. EXPERIMENTAL METHODS



Figure 2.4 (a) Distribution of residence times between two jumps, (b) corresponding distribution of jump frequency.



Figure 2.5 The relationship between relaxation rate  $1/T_1$  and reciprocal of the correlation time  $\tau_c$ . The  $1/T_1$  shows a peak at  $1/\tau_c = \omega_L$ .

# Chapter 3 Experimental apparatus

In this chapter, details of the apparatus and data-acquisition system will be described.

## 3.1 Production and implantation system

The experimental setup used for the present  $\beta$ -NMR detection of <sup>12</sup>B is shown in Fig.3.1 and Fig.3.2. Short-lived <sup>12</sup>B nuclei were produced through <sup>11</sup>B(d,p)<sup>12</sup>B reaction initiated with a deuteron beam of 1.5 MeV accelerated by the 4.75 MV Van de Graaff accelerator at Osaka University. The recoil nuclei ejected to the recoil angles form 37.5° to 42.5° relative to the incident beam direction selected by a Cu collimator were implanted into a Si sample. In order to maintain the nuclear polarization and to detect  $\beta$ -NMR, the external magnetic field  $H_0$  (6.0000 kOe) was applied perpendicular to the reaction plane, which is parallel to the spin polarization along the whole flight path of the recoil nuclei and on the implantation medium.

The target (Fig.3.1–(c)) for the production of <sup>12</sup>B was natural boron (natural abundance <sup>11</sup>B: 80.2 %, <sup>10</sup>B: 19.8 %) and was evaporated by vacuum evaporation technique onto a Ta plate (0.5 mm thickness) using the electron-bombardment equipment. The target was mounted on a target holder, the surface of which was exposed to the deuteron beam with the glancing angle of 5°. The target holder was insulated for monitoring the target current, which was about 15  $\mu$ A. The target holder was cooled by a water flow.

The typical target thickness was about 150  $\mu$ g/cm<sup>2</sup>, which was twice thicker than the range of the recoil nuclei in the recoil direction. Consequently, the energies of the recoil nuclei ejected from the target were spread from 0 to the maximum recoil energy (450 keV). So, the implantation depth was also distributed from 0 to the maximum range of 1  $\mu$ m. Thus the density of the <sup>12</sup>B in Si sample was almost homogeneous and the corresponding dose rate was about 10<sup>8</sup> ion/cm<sup>3</sup>/s (total dose for a sample was about 10<sup>12</sup> ion/cm<sup>3</sup>), which is much less than the one of the doped B in the present samples (see §3.6).

In the magnetic field, no magnetic material was placed for not to disturb the homo-

Table 3.1 Properties of the rf coil:

Turn number	$6 \times 2$
Inductance	$3.6 \ \mu H$
Intensity at the center of the coil	2.5 Oe/A

geneity of the field. The chamber was made of copper except for  $\beta$ -ray windows (Al 200  $\mu$ m). As a result, the inhomogeneity of the magnetic field was less than approximately  $10^{-5}$  in the sample volume.

#### **RF** system 3.2

The rf oscillating magnetic field was applied for the detection of the NMR by an rf coil which is the square-shaped Helmholtz type as shown in Fig.3.3. It was made of Cu wire (0.5 mm-diameter). In order to insulate each turn of the coil, the Cu wire was threaded with (aluminous) ceramic tubes. The coil was fixed on a coil holder. The properties of this coil are listed in Table 3.1.

The rf control system for the NMR are shown in Fig.3.4. Two rf signals from two frequency synthesizers were mixed to generate frequency modulated rf. The one for the carrier frequency can be controlled by the supervising computer for its frequencies within 100  $\mu$ s. And the other generates the frequency-modulated rf through the voltage controlled oscillator (VCO)."

When an rf start pulse was sent from the PC through the parallel I/O interface, the carrier frequency data was sent simultaneously to the fast switching synthesizer. To avoid the disturbance at the transient period for the frequency switching, the rf gate signal was triggered after  $\sim 300 \ \mu s$  delayed from the start pulse. By the rf gate pulse, the frequency modulation for the other generator was started. These two rfs were mixed to obtain a required frequency, as shown in Fig.3.5. Thus synthesized rf signal was amplified by a preamplifier, and then transmitted to a 1000-W power amplifier at the experimental hall after checked for its frequency, wave form and amplitude with a frequency counter and an oscilloscope.

The amplified rf power was fed into the LC resonance circuit (fig.3.6) so as to be supplied to the rf coil effectively. For an impedance matching, a transformer was installed at the first stage of the resonance circuit. The LC circuit was tuned by a variable vacuum

3.3.  $\beta$ -ray counting system

capacitor. The intensity of the rf-field, *i.e.*, the voltage applied to the coil, was monitored at the test point divided by small capacitors. The maximum intensity obtained by the present rf system was about 20 Oe at the center of the coil. Typical rf wave form is shown in Fig.3.6. As shown in the figure, the Q value at the present rf system was about 10.

#### $\beta$ -ray counting system 3.3

 $\beta$  rays were detected by two sets of counter telescopes placed at 0° (up) and 180° (down) relative to the external magnetic field  $H_0$ . Each counter telescope consisted of two plastic scintillation counters; a thin 1.5 mm-thick counter ( $\Delta E$ -counter) and 7 mmthick counter (E-counter).  $\beta$  rays were identified by the coincidence logic of these two counters. A thin Cu plate (0.5 mm) was placed between the  $\Delta E$ -counter and the Ecounter in order to reject low energy  $\beta$  rays that came from background activities. The geometry of the counters is shown in Fig.3.7.

The counters were set outside of the chamber facing the  $\beta$ -ray windows. The solid angel covered by the counter system was about 0.5 steradian. In this thesis no correction for this finite solid angle was made, because it is about 3 % and does not seriously affect the results compared with statistical errors. To avoid any gain shifts of photomultiplier tubes due to the strong magnetic field, photomultiplier tubes were shielded by steel and  $\mu$ -metal tubes, and were placed away from the magnet behind a steel-wall.

The present data taking system is shown in Fig.3.8. Anode pulses of the photomultiplier tube (R329-02, E934/Hamamatsu) were converted to a fast logic signal by discriminators. The threshold level was adjusted to reject low energy backgrounds and electric noises. The pulse widths were 10 ns and 20 ns for  $\Delta E$  and E counters, respectively. The true signal was provided by the coincidence logic  $\Delta E \cap E$ . Thus obtained two logic signals were counted by a CAMAC scaler. The scaler data were transferred and stored by PCs in each bin.

Typical  $\beta$ -ray time spectrum is shown in Fig.3.9. It is shown that the contamination from the background activities was less than 0.5 % of the total counts.

## 3.4 Timing program of the experiment

In order to reject unwanted backgrounds and to see the relaxation of the nuclear polarization, the pulsed beam method was employed, *i.e.*, the counting period was separated from the beam-bombardment period. In order to make this pulsed beam method

possible, a beam chopper system was used, where the electric beam deflector was employed. All these the electric beam chopper, the rf system and the  $\beta$ -ray counting system was supervised by PCs. The timing program is shown in Fig.3.10(a). A beam cycle composed three periods. The durations of the beam-bombardment period, the rf-period and the counting period were 25 ms, 15 ms (typical) and approximately 40 ms, respectively. Total duration of one cycle was at least 80 ms, with which conditions the number of  $^{12}B$ produces in the previous cycle reduced to 1/16. A set of cycles (beam / rf / counting) were repeated with changing the rf frequencies until necessary counting statistics were accumulated, in order to avoid a possible long-time fluctuation of the beam condition. The computer programs are listed in APPENDIX D

In order to destroy the polarization in an appropriate frequency range, the rf frequencies were modulated linearly 5 times in one rf period (Fig.3.10-(b)). In  $\beta$ -NQR measurements, a set of the rfs which correspond to the two transition frequencies between sublevels were also repeated sequentially. In  $\beta$ -NQR measurement, the rf period of 15 ms was needed; 1.2 ms (one modulated-rf time) + 0.3 ms (a frequency-switching time)]  $\times$  10 repetition. In the conventional  $\beta$ -NMR measurement, however, when modulation duration of 1.2 ms is adopted, the total duration becomes  $1.2 \text{ ms} \times 5$  repetition = 6 ms. Because it is desirable to keep the same timing program, in this case, rf-off (blank) time of 9 ms was inserted following actual rf-applying time of 6 ms to make the total rf period the same as that for  $\beta$ -NQR..

At the end of the rf period, the  $\beta$ -ray counting time was started. The counting period was divided into eight sections to observe the relaxation phenomena. By use of Eq.2.4, the polarization change for the *i*-th section was deduced as

$P_i$	=	$\frac{R_i/R_{i,\text{off}}-1}{R_i/R_i - r_i + 1},$	(3.1)
$R_i$	=	$N_i(0^\circ)/N_i(180^\circ).$	(3.2)

('off' means the rf with frequency far off (10 MHz) from the resonance frequency.)

#### Temperature control system 3.5

The temperature of the sample was kept constant by a temperature control system. The controlled temperature range was about 100 K to 300 K with  $LN_2$  (liquid  $N_2$ ) as a coolant, and about 300 K to 750 K without  $LN_2$ .

The diagram of this system is illustrated in Fig.3.11. A sample holder made of Mo

3.6. SAMPLE PREPARATION

Table 3.2 Samples used in the present experiment.

			Dopant	Production
Sample No.	Type	Dopant	density $(cm^{-3})$	process
1	р	В	$3 \times 10^{14}$	FZ
2	р	В	$7 \times 10^{17}$	FZ
3	n	Р	$6 \times 10^{14}$	FZ

was extended from a Cu-block in which a heater (30 W) was installed. The sample system was well isolated from the room temperature by two thermal shields. To keep temperature constant, the on/off control method was used; where heater was on at a certain temperature, heater was off above the temperature. Since it is not the sample but the Cu-block which shows fast response to a temperature change, a thermocouple (Chromel-Alumel of  $\phi 0.3 \text{ mm}$ ) was installed for temperature control on the surface of the Cu-block. The temperature of the sample was measured with another thermocouple at the end of the sample holder. Considering the temperature gradient of the sample, the stability of the control system and the accuracy of the temperature measurement, the total errors of the measured temperature was estimated to be about 1.2 K at the temperatures under 600 K and about 2.5 K at the temperatures above 600 K.

#### Sample preparation 3.6

Three kinds of the samples were prepared. Two of them were B doped p-type silicons with electric resistance of 40–60  $\Omega$ cm and 0.07–0.13  $\Omega$ cm. The other is P doped n-type crystal with 8–10  $\Omega$ cm. The concentrations of dopants were about  $3 \times 10^{14}$  B/cm<sup>3</sup>,  $7 \times 10^{17}$  $B/cm^3$  and  $6 \times 10^{14} P/cm^3$ , respectively [Irv62].

The size of the samples was  $17 \times 17$  mm cut from the Si wafers (300  $\mu$ m thickness). The surface was lapped mechanically and was etched in an etchant, which is the mixture of 6 parts of HNO<sub>3</sub> (70 %), 1 part of HF (50%) and 2 parts of CH<sub>3</sub>COOH (100 %) solution in volume, for mirror-like smooth surface [Syo76]. As a result of etching, the thickness of the samples became about 200  $\mu$ m. Just before using, it was rinsed with dilute HF solution ( $\sim 2.5$  %) and pure water.

3.6. SAMPLE PREPARATION

- (a) Beam Transport system Reaction and NMR Chamber Overview of the  $\beta$ -NMR chamber Electric Doublet Beam Q-Magnet Deflector Beam Chopper NMR Magnet d<sup>+</sup> beam H<sub>0</sub> from V.d.G. Experimental hall Shield Analyzer room Magnet Pole Piece (b) Reaction and NMR Chamber Thermal Shields (with Heater) Si Sample Collimator **Plastic Scintillators** d<sup>+</sup> beam Boron Target Recoil Catcher (Si) (c) Boron Target Target area RF. Coil (thickness:  $\sim 150 \,\mu g \,/ \,cm^2$ ) 15 mm Ta substrate (0.5 mm thickness) Figure 3.2 The overview of the  $\beta$ -NMR chamber. <−10 mm→ -15 mmwere detected by the scintillation counters.
  - Figure 3.1 Sketches of (a) the beam transport system, (b) the recoil-angle selection, and (c) the boron target.

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The target was bombarded by the  $1.5 \text{ MeV d}^+$  beam. The polarized nuclei obtained by selecting its recoil angle were implanted into the sample of Si. Their spins were manipulated by rf-fields. The  $\beta$ -rays





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respectively.

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Figure 3.4 Block diagram of the rf control system. The frequency and the timing of the pulses was controlled by the PC. The electric circuits of 'rf mixing circuit' and 'resonator' are shown in Fig.3.5 and Fig.3.6,

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## Figure 3.5 Diagram of the rf mixing circuit. The rfs from the two frequency synthesizers are mixed and filtered.

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4791 MHz

onance circuit.

42

Q-curve observed at the voltage monitor point.



Figure 3.6 Resonator-parallel LC resonance circuit and a Q-curve of this res-







(b) Sizes of the detectors



•











46

		47
	Time	
quency-1	frequency-2	
40ms		
period 5 ms		
1		
-15 ms		

Figure 3.10 (a) Timing program of the pulsed beam method. (b) Two rf applying techniques were used in this experiment.



Figure 3.11 (a) Equipment for temperature control. Heat generated by the heater flows to the  $(LN_2)$  dewar. (b) Block diagram of temperature control system. External resister was used for supplying low power constantly, if needed.

# Chapter 4 Results

To determine implantation sites of <sup>12</sup>B and to study dynamics of the defects annealing, following  $\beta$ -NMR measurements were performed;

- NMR spectra at the Larmor frequency (§ 4.2),
- $\beta$ -NQR spectra (§ 4.3),
- spin-lattice relaxation time  $(\S 4.4.1)$
- temperature dependence of the fraction of each implantation site  $(\S 4.4.2)$ ,
- jumping effect of the nonsubstitutional B nuclei (§ 4.5),
- other measurements for a newly detected resonance  $(B_x)$  (§ 4.6).

Three Si samples with different concentration of dopant were prepared; Sample No.1:  $3 \times 10^{14}$  B/cm<sup>3</sup>, Sample No.2.:  $7 \times 10^{17}$  B/cm<sup>3</sup>, Sample No.3:  $6 \times 10^{14}$  P/cm<sup>3</sup> (§ 3.6). For these three samples, results were similar except for jumping rate and spin-lattice relaxation time. So, the descriptions will be focused mainly on the low density p-type Si sample.

The reaction polarization was determined to be  $-11.3 \pm 0.2$  %, from the  $\beta$ -NMR on <sup>12</sup>B implanted in an annealed Pt (thickness of 15  $\mu$ m), since Pt is known to be a good media for maintaining nuclear polarization.

#### Total maintained polarization of <sup>12</sup>B in Si 4.1

The total maintained polarization of <sup>12</sup>B in Si was measured using a widely frequency modulated rf ( $\nu = \nu_L \pm 200$  kHz). Fig.4.1 (a) shows thus obtained total maintained polarization of <sup>12</sup>B. Since the reaction polarization is determined to be  $-11.3 \pm 0.2 \%$ from the measurement of <sup>12</sup>B in Pt, almost all the polarization of implanted <sup>12</sup>B is kept at temperatures below 260 K and above 550K. Above 260 K, the fraction of the detectable polarization decreases rapidly and reached approximately 60 %. In the temperature



• total maintained nuclear polarization by use of widely modulated rf (§ 4.1),

range from 300 K to 450 K, the fraction was kept constant (60 %), and increases rapidly again to 100 % at about 500 K. Similar results were obtained for other two samples No.2 and No.3 as shown in Fig.4.2(a) and (b).

In order to check that all the <sup>12</sup>B which maintained the polarization was manipulated by the present frequency range  $\nu = \nu_L \pm 200$  kHz, polarization was also deduced from the ratio of the counting rate in up and down counters as described blow. Since the full polarization was detected by the  $\beta$ -NMR at 100 K or 550 K, the polarization was totally destroyed by an rf at these temperatures. Therefore, the maintained polarization at any temperature can be obtained by comparing the counting rate ratio at the temperature with that at 100 K, where the polarization completely destroyed with rf on

$$2AP = \frac{(U(T)/D(T))_{\text{off}}}{(U(100 \text{ K})/D(100 \text{ K}))_{\text{on}}} - 1.$$

where U(T), and D(T) are the  $\beta$ -ray counts at the temperature T. Subscripts shows whether the rf is on or off. The result is shown in Fig.4.1 (b). Thus obtained polarization was almost the same as the result obtained by use of the direct  $\beta$ -NMR detection at temperature T. From the analysis of the result, it is concluded that all the resonance frequencies are covered within the present frequency range  $\nu = \nu_L \pm 200$  kHz. The similar results were obtained for other samples as well.

## Resonance line of <sup>12</sup>B nuclei at the substitution-4.2 al sites $(B_s)$

As mentioned in §1.1, McDonald and McNab determined that only the <sup>12</sup>B nuclei in the substitutional site contributed to the sharp resonance at the Larmor frequency [MM76]. In the present experiment, NMR spectra at the Larmor frequency which come from the substitutional <sup>12</sup>B were observed at various temperatures (100 K  $\leq T \leq$  750 K). The experimental conditions are listed in Table 4.1. Typical NMR spectra are shown in Fig.4.3-4.5. Remarkable change was shown in the amplitude of the spectra with increasing temperature.

The spectra were fitted with Lorentzians to extract resonance amplitude. The fraction of the substitutional <sup>12</sup>B was determined from the amplitude of the resonance. The rf field  $H_1$  of about 0.5 Oe was strong enough to saturate the spectra. The fraction of  $(^{12}B_s)$  was defined as the resonance amplitude normalized by the reaction polarization, which is the full polarization of  ${}^{12}B$  in Pt.

The results are shown in Fig.4.6. Below 100 K, the fraction is almost zero. As the

#### 4.3. $\beta$ -NQR SPECTRA (B<sub>X</sub>, B<sub>NS</sub>)

Table 4.1 Experimental conditions for the Larmor resonance.

External magnetic field Beam bombardment t rf time

> Counting time rf intensity  $(H_1)$ rf modulation Crystal orientation

temperature goes up, the substitutional fraction gradually increases to reach 80 % at 650 K. The slope of the increase seems to change slightly at 400  $\sim$  450 K as is seen in the literature as well.

The observed line widths ( $\sim$ 850Hz FWHM) were broader than the natural width (Table 1.2) due to the relatively intense  $H_1$  field, and were consistent with the present power broadening  $\gamma H_1/2\pi \approx 760$  Hz (FWHM).

The polarization was observed as a function of time and the spin-lattice relaxation time  $T_1$  was obtained by  $\chi^2$ -fitting analysis. The results are shown in Fig.4.6. Relaxation of the polarization was not observed at any temperatures and dopant density. Thus, the spin-lattice spin relaxation time  $T_1$  was long enough compared with the nuclear lifetime, expected from the low conduction electron density. (Fig.4.11).

# 4.3 $\beta$ -NQR spectra (B<sub>x</sub>, B<sub>ns</sub>)

The typical spectra are shown in Fig.4.6-4.9. Two resonance lines are clearly seen in the observed  $\beta$ -NQR spectra around  $\nu_{Qsplit} = 270$  kHz and 0kHz. The sharp resonance at  $\nu_{Qsplit} = 270$  kHz comes from the nonsubstitutional <sup>12</sup>B (B<sub>ns</sub>)

$(H_0)$	6 kOe
ime	25 ms
	$15 \mathrm{ms}$
	(on: 6 ms / off: 9ms)
	40 ms
	0.5
	no modulation
	$\langle 110 \rangle \parallel H_0$

 $\beta$ -NQR spectra were observed at the frequency range from  $\nu_{Qsplit} = 0$  kHz to 400 kHz. Here, the  $\nu_{Qsplit}$  means the full span between the two resonance-frequencies split due to quadrupole interaction, or twice of the distance between the Larmor frequency and one of the resonance frequency. Experimental conditions are tabulated in Table 4.2.

#### CHAPTER 4. RESULTS

4.4. TEMPERATURE DEPENDENCE OF THE FRACTION AND THE SPIN-LATTICE RELAXATION

Table 4.2	Experimental	conditions f	for	$\beta$ -NQR spectra	
an era con a constant		A A WHY CAN A W HAR A		p a que opecere	· · · ·

External magnetic field H	61-00	
External magnetic field $H_0$	0 KOe	
Beam bombardment time	25 ms	
rf time	15 ms	
	(on: 12 ms / off: 3 ms)	
Counting time	40 ms	
rf intensity	1 Oe	
rf modulation	$\pm$ 10 kHz in $\nu_{Qsplit}$	
Crystal orientation	$\langle 110 \rangle \parallel H_0$	

which have an (111) axial symmetry, which have been found also by Fischer *et al.* by the conventional  $\beta$ -NMR [FSD+92].

The broad resonance around  $\nu_{Qsplit} = 0$  kHz was detected for the first time. This resonance corresponds to the missing fraction of <sup>12</sup>B implanted in Si, which was predicted from the previous experiments by Minamisono et al. [MNDA83]. Although the resonance line overlapped with the sharp resonance line for the substitutional <sup>12</sup>B, the two resonances could be separated since their line widths are very much different. From now on, the <sup>12</sup>B nuclei contributed to this newly detected broad resonance is labeled as  $^{12}B_x$ , which will be discussed later in § 4.6.

For the resonance for  $B_{ns}$ , it have been known that the quadrupole interaction has the (111) axial symmetry with the coupling constant  $|eqQ/h| = 2\nu_Q/3 = 360(15)$  kHz [SFD+92]. We confirmed the (111) symmetry. As shown in Fig.4.10-(a), the  $\beta$ -NQR spectra were observed for three crystal orientations, *i.e.*,  $\alpha = 0^{\circ}$  ((001)), 22.5° and 45°  $(\langle 011 \rangle)$ , where  $\alpha$  is angle between  $H_0$  and  $\langle 001 \rangle$  axis in the  $\{100\}$  plane. The resonance frequency for  $B_{ns}$  is far from the Larmor frequency at  $\alpha = 45^{\circ}$ . It comes closer to the Larmor frequency as  $\alpha$  decreases, because all the four (111) axis become to form the magic angle with the external magnetic field  $H_0$ . The obtained  $\nu_{Qsplit}$  is shown as a function of  $\alpha$  in Fig.4.10 (b). Assuming the asymmetry parameter  $\eta = 0$ , the fit to the Eq.2.11 proves that  $B_{ns}$  nuclei are at the site where q is parallel to the (111) axis with its quadrupole coupling constant |eqQ/h| of 364(7) kHz.

While the  $B_{ns}$  resonance was clearly observed at 150 K and 250 K as seen Fig.4.6-4.9, it disappeared at 350 K. This temperature dependence will be described later in § 4.4.

Table 4.3 Experimental conditions for measurement of fractions.

		_
Experiment		
External magnetic field $H_0$		
Beam bombardment time		
rf time		
A CAPACITY AND A STATE	(on:	1
Counting time		
rf intensity		
rf modulation		
Crystal orientation		

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From these  $\beta$ -NMR spectra, it was revealed that there are at least three implantation sites of  ${}^{12}B - B_s$ ,  $B_{ns}$ , and  $B_x$ .

## Temperature dependence of the fraction and 4.4 the spin-lattice relaxation time for each implantation site

corresponding to each site completely.

for B<sub>ns</sub> for  $B_s + B_x$ 6 kOe 25 ms 15 ms15 ms2 ms / off: 3 ms) (on: 6 ms / off: 9 ms) 40 ms 5 Oe  $\pm$  100 kHz in  $\nu_{Qsplit}$  $\langle 110 \rangle \parallel H_0$ 

Fractions of  $B_{ns}$  and  $B_x$  sites as well as the  $B_s$  site were measured as a function of temperature. The fraction of B<sub>s</sub> was determined from the amplitude of the sharp resonance at Larmor frequency as is already described in § 4.2. The fractions of  $B_{ns}$  were determined from the amplitude of the peak at  $\nu_Q = 270$  kHz in the  $\beta$ -NQR spectra using a wide rf modulation  $\nu_{Qsplit} = 270 \pm 100$  kHz for the crystal orientation (110) ||  $H_0$ . Sum of the fractions for  $(B_s + B_x)$  was determined from the polarization destruction method in the  $\beta$ -NMR with a wide rf modulation ( $\nu = \nu_L \pm 50 \text{ kHz}$ ). Experimental conditions are tabulated in Table 4.3. Applied rf intensity,  $H_1$ , was enough to destroy the polarization

### 4.4.1 Spin-lattice relaxation time $T_1$

Before describing the result of the fractions, time-dependent phenomena must be clarified. In all  $\beta$ -NMR measurements, the time-development of the polarization was also measured to extract the relaxation time. Experimental conditions for  $(B_s + B_x)$ and  $B_{ns}$  measurements were the same as mentioned above (Table 4.3). For  $B_s$ , several data points near the Larmor frequency were summed up.

Although no significant relaxation was seen for  $(B_s + B_x)$  and  $B_s$ ,  $T_1$  for  $B_{ns}$  around 300 K was very fast as seen in Fig.4.12-4.14. All these time dependence of the polarization were analyzed by  $\chi^2$ -fitting using exponential decay. Resultant relaxation rates for  $B_s$  or  $(B_s + B_x)$  are shown in Fig. 4.11. The relaxation rate  $1/T_1$  and the initial polarization, which is defined by the polarization that was at the production time, are shown in Fig.4.15 – Fig.4.17. From the figures, fixed fraction of  ${}^{12}B$  is located in  $B_{ns}$  site and the reduced polarization of the  ${}^{12}B_{ns}$  nuclei is due to the polarization reduction by short relaxation time  $T_1$ .

While the spin-lattice relaxation time  $T_1$  becomes shorter as the temperature increases, the fraction of B<sub>ns</sub> is almost constant of about 35 % below 325 K. The polarization for B<sub>ns</sub> nuclei was completely disappeared above 350 K, because of the too short relaxation time.

It should be noted that the behavior of the relaxation time with temperature for the highly doped sample is slightly steeper than the one for the sample with lower density of dopant.

#### 4.4.2 Fraction for each location

The observed polarization during the counting time of 40 ms is shown in Fig.4.18-4.20 (a). Inner consistency of the present procedure was checked by comparing the sum of the polarizations change of the ones for  $B_s$ ,  $B_x$  and  $B_{ns}$  with the total maintained polarization. Fig.4.18-4.20 (b) shows the fraction of each implantation site. The B<sub>ns</sub> fractions are the one deduced as described in  $\S4.4.1$ . The B<sub>x</sub> fraction was obtained by subtracting  $B_s$  fraction from the sum of the  $(B_s + B_x)$  fraction.

As seen in Fig.4.18–4.20 (a), the total amount for the  $(B_s + B_x)$  fraction stays nearly constant in the temperature range from 100 K to 450 K, although the B<sub>s</sub> increases with temperature. It may imply that  ${}^{12}B$  in the  $B_x$  site, which is the majority at the lower temperature, seems to be converted into B<sub>s</sub> site at higher temperatures.

While almost 100 % of polarization of <sup>12</sup>B is detected at temperature below 260 K, the

### 4.5. JUMPING EFFECT OF BNS NUCLEI

"total" polarization decreases to about 60 % above 300 K. This decrease is mainly because of the decrease of the  $B_{ns}$  component because the fraction of  $(B_s + B_x)$  is constant. At temperatures above 260 K, the observed polarization for the B<sub>ns</sub> nuclei rapidly decreases and disappears at a temperature higher than 350 K. Although the polarization of B<sub>ns</sub> couldn't be observed above the temperature, it is natural to conclude that even at the temperatures higher than 350 K, about 35 % of implanted <sup>12</sup>B nuclei is located in the  $B_{ns}$  site and its polarization is destroyed due to the fast  $T_1$  for  $B_{ns}$  nuclei.

At 450 K, the  $(B_s + B_x)$  fraction starts to increase and completely recovers to 100 % at 550 K, while at higher temperatures above 650 K, the fraction of B<sub>s</sub> is reached to about 80 % and seems to be saturated (the measurement in this temperature range was performed only on the low doped p-type Si).

## 4.5 Jumping effect of B<sub>ns</sub> nuclei

It has been suggested by Ackermann *et al.* ( $\S$ 1.1) that the direction change of *q*-axis was caused by thermal activated atomic jumps. In order to see the effect caused by the direction change of q-axis at the location of  $B_{ns}$  atom, the polarization change was measured by applying just one resonance frequency among the two frequencies split by the quadrupole interaction. When only one transition frequency is applied, the nuclear polarization is just partially destroyed without jumping effect. If the direction of qaxis did not change at least within the rf period, the polarization change is expected to be about 1/4 of that in the case of complete destruction, assuming zero initial spin alignment. This situation is illustrated in Fig.4.21.

As shown in Fig.4.22-4.24 by B<sub>ns</sub>(H or L), at low temperatures below about 200 K, just 1/4 of the total  $B_{ns}$  is observed for the single transition, which implies the nuclei are indeed immobile at least in the time range of the present experiment (  $\sim 40$ ms). Above 200 K, however, the polarization change increases as the temperature and reached total B<sub>ns</sub> at about 275 K, which implies the direction change of the q-axis due to the jump between four identical locations. Above the temperature, it rapidly reduced to zero coincident with the decrease of the total  $B_{ns}$  signal, because of its fast spin-lattice relaxation time. This phenomena due to fast thermal jumping was the one also reported in the previous experiment by Frank et al. [FDE+94]. However, they couldn't deduce the jumping rate, mainly because of the lack of the knowledge on the polarization relaxation and the total polarization for B<sub>ns</sub>. The jumping rate deduced from the present result will be discussed in the next chapter.

#### Other features for $B_X$ 4.6

In order to understand the nature of the broad resonance from  $^{12}B$  in  $B_x$  site nuclei, three other measurements were performed.

(1) Fig.4.25 shows three kinds of polarization changes for  $B_x$ ; the polarization  $(P_x)$ was measured by the  $\beta$ -NQR method with  $\nu = \nu_L \pm 35$  ( $\Delta \nu = 25$  kHz), the other two  $(P_x(H \text{ or } L))$  were measured when only on the higher or lower side of the Larmor frequency was applied ( $\nu = \nu_L - 35 \text{ or } + 35 \text{ kHz} (\Delta \nu = 25 \text{ kHz})$ ). Since  $P_x(H \text{ or } L)$ is about 1/4 of  $P_X$ , the broad resonance around the Larmor frequency is due to static electric quadrupole interaction on the same reason discussed for  $B_{ns}$  in § 4.5. If it is due to any other static shift of magnetic field, the  $P_X(H \text{ or } L)$  has to be about half of  $P_X$ . If it is due to the dynamic shift, it will be the same as  $P_X$ .

(2) The spectra for  $B_x$  at room temperature (~300 K) were measured at two different crystal orientations,  $\angle (\langle 001 \rangle \cdot H_0) = 22.5^\circ$ , and 45° in {100} plane, as seen in Fig.4.26. No angular dependence of spectra was observed. Therefore, it can be concluded that the principal axis of the quadrupole interaction is randomly distributed.

(3) As seen in  $\beta$ -NQR spectra (Fig.4.6), the resonance from  $B_x$  nuclei is narrower at higher temperatures. To see the narrowing of the spectrum more clearly, the  $\beta$ -NMR spectra were analyzed by  $\chi^2$ -fitting assuming Gaussian distribution of  $\nu_{Qsplit}$ . In this analysis, data points for  $\nu_{Qsplit} < 10$  kHz were rejected, since these data may be affected from the  ${}^{12}B$  in  $B_s$  site. The obtained width are plotted as a function of temperature in Fig.4.27.

At  $T \leq 200$  K the widths are constant (about 45 kHz). As increasing temperature from 200 K to 400 K, the width becomes narrower and reaches to approximately 20 kHz at 400 K. Above 400 K, the width is kept constant.



maintained polarization.

Figure 4.1 (a) NMR effect of <sup>12</sup>B in p-Type Si  $(3 \times 10^{14} \text{ B/cm}^3)$ . The experimental conditions were  $H_0 = 6$  kOe, and  $f = 4591 \pm 200$  kHz,  $H_1 \sim 10$  Oe. (b) Maintained polarization estimated from up/down count rate ratio. (See text.) (c) Deviations of NMR effects from







Figure 4.3 NMR spectra at the Larmor frequency of <sup>12</sup>B in p-type Si  $(3 \times 10^{14})$ B/cm<sup>3</sup>). The statistical error of each data point is about  $\pm 0.5$  %. The solid line is the Lorentzian curve best fit to each spectrum.
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Figure 4.5 NMR spectra at the Larmor frequency of <sup>12</sup>B in n-type Si  $(6 \times 10^{14}$  $P/cm^3$ ). The statistical error of each data point is about  $\pm 0.5$  %. The solid line is the Lorentzian curve best fit to each spectrum.





Figure 4.6 Fractions of the substitutional  $^{12}B$  as a function of temperature.  $\beta$ -NQR spectra at (a) 350 K, (b) 250 K and (c) 150 K are given. Fractions are normalized by the total polarization obtained through nuclear reaction.

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Figure 4.7  $\beta$ -NQR spectra of <sup>12</sup>B in p-type Si (3 × 10<sup>13</sup> B/cm<sup>3</sup>). The width of the frequency modulation for  $\nu_{Qsplit}$  was  $\pm$  10 kHz.







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 $v_{Q \text{ split}} (kHz)$ 

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Figure 4.9  $\beta$ -NQR spectra of <sup>12</sup>B in n-type Si (6 × 10<sup>14</sup> P/cm<sup>3</sup>). The width of the frequency modulation for  $\nu_{Qsplit}$  was  $\pm$  10 kHz.







nuclei.



Figure 4.11 Spin-lattice relaxation rate  $1/T_1$  for (a) B<sub>s</sub> nuclei and (b) (B<sub>s</sub> + B<sub>x</sub>)









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the data.

Figure 4.13 Spin-lattice relaxation times for  $B_{ns}$  nuclei in p-type Si (7  $\times$  10<sup>17</sup>  $B/cm^3$ ). The solid curves are the exponential function best fit to

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Figure 4.15 Initial polarization at the production time, and spin-lattice relaxation time for the B<sub>ns</sub>nuclei in p-type Si  $(3 \times 10^{14} \text{ B/cm}^3)$ .



Figure 4.16 Initial polarization at the production time, and spin-lattice relaxation time for the  $B_{ns}$ nuclei in p-type Si (7 × 10<sup>17</sup> B/cm<sup>3</sup>).



Figure 4.17 Initial polarization at the production time, and spin-lattice relaxation time of the  $B_{ns}$ nuclei in n-type Si (6 × 10<sup>14</sup> P/cm<sup>3</sup>).







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CHAPTER 4. RESULTS





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Figure 4.21 Jumping effect for an  $\beta$ -NMR measurement.

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Figure 4.23 Enhancement of NMR signal for  $B_{ns}$  nuclei in p-type Si  $(7 \times 10^{17}$  $B/cm^3$ ). Experimental conditions, except for the rf frequency, were same as the measurement of  $B_{ns}$  fraction.

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CHAPTER 4. RESULTS

NMR signals of  $B_{ns}$  in Si (n-type:  $6 \times 10^{14}$  P/cm<sup>3</sup> No.3) • Total amount of B<sub>ns</sub>  $\circ$  B<sub>ns</sub>(H) High frequency side (v<sub>L</sub> + 85 kHz < v < v<sub>L</sub> + 185 kHz)  $\square$  B<sub>ns</sub>(L) Low frequency side ( $v_L$  - 185 kHz <  $v < v_L$  - 85 kHz) Asymmetry Change (2AP; %) 10 8 Ŧ . 6 4 2 0 200 300 100 400 Temperature (K) 2.0F Ratio to total B<sub>ns</sub> 1.5 1.0 0.5 0.0 200 300 100 400 Temperature (K)



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Figure 4.25 Asymmetry change of <sup>12</sup>B settled at  $B_x$  at temperature of 150 K. Closed circles represent the change in the rf frequency range of  $\nu_{Qsplit} = 70 \pm 50$  kHz by use of the  $\beta$ -NQR method. Open circles and closed squares represent the change in the case of single rf, 70 + 50 kHz and 70 - 50 kHz respectively







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CHAPTER 5. DISCUSSIONS

### 5.2. JUMPING EFFECT OF THE ATOMS

## Chapter 5

## Discussions

In the previous chapter, it was disclosed that there are three components for the implantation site of  ${}^{12}B$  in Si: the substitutional site of Si ( $B_s$ ), the nonsubstitutional site with (111) axial symmetry  $(B_{ns})$ , and the site which gives the broad resonance around the Larmor frequency  $(B_x)$ . It is evident that the  $B_{ns}$  and  $B_x$  are originated from some defects of the lattice but their atomic configurations have not been known yet. In the following section, we will discuss the atomic configuration and characters of B<sub>ns</sub> from the experimental results. In section 2, we will discuss about the implantation sites including the  $B_s$  and  $B_x$  sites.

#### The nonsubstitutional site B<sub>ns</sub> 5.1

As described in the previous chapters, the direction of the axial symmetry of  $B_{ns}$  is jumping around with thermal energy. The  $B_{ns}$  are identical with the B<sup>+</sup> defect found by (Watkins's) ESR measurements, however, the microscopic configuration of it is not known certainly. Tarnow made an *ab initio* total energy calculations on the B sites in Si. It was suggested that for the positive-charge state, the lowest energy state is neither simple interstitial B nor bond-centered B, but a substitutional B combined with a Si atom [Tar91] (we denote this configuration as  $(B_s - Si_i)$  (Fig.5.1)). According to this calculation, since substitutional B is singly negative-charged and the interstitial Si is doubly positivecharged, the  $(B_{s}$ -  $Si_i)$  has an attractive coulomb interaction, which cause the slight lattice deformation: as the (111) direction is compressed, the perpendicular directions are expanded as shown in Fig.5.1. This model explains the variation of the direction of (111) axial symmetry by the jumping the Si<sub>i</sub> atom through hexagonal interstitial site to other tetrahedral interstitial site with the activation energy of about 0.6 eV.

In the followings, through the discussion of the present results assuming this model, the validity of it will be examined. In accordance with this model, the present experimental results can be illustrated below. The implanted <sup>12</sup>B loses its energy by atomic collision in crystal and is finally settled in the substitutional site pushing out the Si atom to the interstitial site. Then the lattice is compressed by the coulomb attraction between them. Thus formed dumbbell structure is assumed to be the similar one as is predicted by Tarnow. With the thermal energy, the interstitial Si is jumping around the <sup>12</sup>B, not the substitutional <sup>12</sup>B is jumping. By this jumping, the direction of the field gradients varies its axis.

In the following two sections, the observed relaxation and recovery of the polarization are explained in terms of the atomic jump of this  $B_{ns}$  configuration.

### 5.2 Jumping effect of the atoms

As shown in the previous chapter, it was revealed that the reduction of the observed  $B_{ns}$  polarization above 250 K is due to the fast spin-lattice relaxation. In this section, this relaxation will be discussed quantitatively.

The following four processes should be considered as possible cause of the spin-lattice relaxation:

- electric field gradient  $(1/T_{1q})$ ;
- dipole field  $(1/T_{1d})$ ;
- $(1/T_{1e});$
- paramagnetic field or electric field gradient  $(1/T_{1t})$ .

Thus the relaxation is expressed by,

$$\frac{1}{T_1} = \frac{1}{T_{1q}} -$$

field gradient [(1)] can be the dominant process for the relaxation.

(1) the interaction between the electric quadrupole moment of  ${}^{12}B$  and a time-varying

(2) the interaction between the magnetic dipole moment of  ${}^{12}B$  and a time-varying

(3) the interaction of the  ${}^{12}B$  with the conduction electron of the host silicon crystal

(4) the trapping of the  ${}^{12}B$  as it diffuses into the low-symmetry site which has a large

$$\frac{1}{T_{1d}} + \frac{1}{T_{1e}} + \frac{1}{T_{1t}}.$$
(5.1)

Under the  $(B_{s}-Si_{i})$  model of Tarnow, the interstitial  $Si_{i}$  is jumping thermally around the B<sub>s</sub> more rapidly with increase of the temperature. This thermal jump is evident from the previous  $\beta$ -NMR studies and our experiment (§ 4.5). This atomic jump leads to the changes of direction of the electric field gradient. Therefore this time-varying electric

As for the relaxation due to the time-varying dipole field [(2)], it has negligible contribution to the relaxation, since the <sup>29</sup>Si which is the only stable isotope that has a magnetic moment ( $\mu = -0.555 \ \mu_N$ ,  $I^{\pi} = 1/2^+$ ) has small natural abundance (4.7 %).

CHAPTER 5. DISCUSSIONS

Contribution from the conduction electron [(3)] is also negligible. The nuclear polarization relaxation rate of silicon host with n-type dopant due to the conduction electrons is given as [Abr63],

$$\frac{1}{T_{1e}} = \frac{64}{3} \gamma_e^2 \gamma_n^2 N \left| \phi(0) \right|^4 \sqrt{2\pi m_1 m_2 m_3 kT}, \tag{5.2}$$

where  $\gamma_e$  and  $\gamma_n$  are the gyromagnetic ratios of the electron and the nucleus, respectively, N is the carrier density,  $m_1m_2m_3$  is the product of anisotropic effective masses, and  $|\phi(0)|^2$  is the electron density at the nucleus. As all the carrier is active above about 100 K, the carrier density is the same as the dopant density in the case of the present experiment. Based on eq.(5.2), the relaxation rate due to conduction electrons for the silicon with the n-type dopant density of  $6 \times 10^{14}$  P/cm<sup>3</sup>, which is the typical one used in the present experiment, is estimated as about 1000 seconds. Actually, the relaxation time of about 100 seconds was observed for the  $^{29}$ Si in n-type Si with  $10^{14}$  cm<sup>-3</sup> dopant density. For the one with  $10^{18}$  cm<sup>-3</sup> dopant density, the relaxation was about several tens seconds ([SW56]). Similar relaxation time is also expected for the <sup>12</sup>B assuming similar electron density at the nucleus, because of the similar gyromagnetic ratio  $\gamma_n$ . Therefore the contribution from conduction electrons cannot be the order of several milli-second observed in the present experiment. In addition, the steep change of relaxation rate as a function of temperature, as seen in Fig.4.15, can not be explained by eq.(5.2) which is proportional to  $T^{1/2}$ .

Lastly, the trapping mechanism [(4)] will be considered. This process should be possible since the temperature dependence of the relaxation rate of the present results shows a exponential function curve as is typical for a thermal diffusion process. However this trapping mechanism can't explain the NMR-signal enhancement (Fig.4.22) which arises at 200 K and persistent to about 250 K where the relaxation is observed.

Then we will treat the fluctuating quadrupole field [(1)] through the atomic jump as the dominant process of the relaxation. Under the assumption of the  $(B_{s}-Si_{i})$  model, using the activation energy  $E_a$  and the jumping frequency  $\nu$ , relaxation rate is expressed as the following equation.

$$\frac{1}{T_1} = \frac{(eqQ)^2}{8\hbar^2} \left\{ k_1(\omega_0) + 4k_2(2\omega_0) \right\} + \text{Constant},$$
(5.3)

$$k_1(\omega_0) = \frac{1}{4} \frac{2\tau_c}{1 + \omega_0^2 \tau_c^2},$$
  

$$k_2(2\omega_0) = \frac{5}{16} \frac{2\tau}{1 + 4\omega_0^2 \tau_c^2},$$

5.2. JUMPING EFFECT OF THE ATOMS

Table 5.1 Activation energy for the atomic jumping of  $(B_s - Si_i)$  pair. (Fit to the polarization data)

			Logarithm of		
		Activation	pre-exponent	Initial	
Sample	Dopant	energy	factor	polarization	$\chi^2$ –Value
number	$(\mathrm{cm}^{-3})$	Ea(eV)	$\log_{10}(\nu_0 (\text{kHz}))$	(%)	(normalized)
1	$3 \times 10^{14} \text{ B}$	$0.46\pm0.07$	$9.2 \pm 1.1$	$3.8\pm0.1$	1.4
2	$7\times 10^{17}~{\rm B}$	$0.49\pm0.06$	$9.6 \pm 0.9$	$3.2\pm0.1$	2.8
3	$6 \times 10^{14} \text{ P}$	$0.47 \pm 0.05$	$9.3 \pm 0.6$	$4.0 \pm 0.1$	2.4

 $\frac{1}{\tau_c} = \nu =$ 

The observed polarizations with the actual experimental timing program were analyzed by the eq.(5.3) which was deduced in § 2.3.3, since the data on the relaxation rate is not precise enough. The detail of the path of the atomic jump and the fitting function used in the analysis is described in APPENDIX C. As a result, the activation energy  $E_a$  and the prefactor  $\nu_0$  are obtained as listed in Table 5.1.

function.

The results from these two analyses agreed within the error. However, the former analysis is more accurate and reliable because of the statistics. So we take former analysis (Table 5.1).

There is no significant difference between the obtained values for the samples of different type and dopant density. This point is seems to contradict with the results from the old experiments. The activation energy  $E_a$  and the prefactor  $\nu_0$  are determined

$$\nu_0 \exp(-\frac{E_a}{kT}).$$

As seen in Fig.5.2~Fig.5.4-(a), the present analysis well reproduces the steep change of the polarization at 275 K  $\sim$ 325 K. As seen in the solid lines in Fig.5.2 $\sim$ Fig.5.4–(b), the observed relaxation rates were also well reproduced with the obtained parameters.

In the next step, the  $1/T_1$  data obtained from the time development of the polarization are fitted with the function 5.3 to see the consistency. The fitting results are shown in Table 5.2 and the doted line in the Fig.5.2 ~ Fig.5.4-(b). The actual  $1/T_1$  data is almost constant below 200 K, while the above mentioned jumping mechanism predicts continuous steep change. This saturation, however, can be naturally understood by a minor contribution from the interactions with the conduction electron and the fluctuating dipole field etc.. So the constant contribution was considered in the actual fitting

5.3. Recovery of maintained polarization

			Logarithm of	
Sample number	Dopant (cm <sup>-3</sup> )	$\begin{array}{c} \text{Activation} \\ \text{energy} \\ Ea(\text{eV}) \end{array}$	pre-exponent factor $\log_{10}(\nu_0 \text{ (kHz)})$	$\chi^2$ –Value (normalized)
1	$3\times 10^{14}~{\rm B}$	$0.37\pm0.13$	$7.7 \pm 1.4$	1.0
2	$7 \times 10^{17} \mathrm{~B}$	$0.46 \pm 0.08$	$9.6 \pm 1.0$	0.81
3	$6 \times 10^{14} \text{ P}$	$0.34 \pm 0.06$	$7.2 \pm 0.8$	2.2

Table 5.2 Activation energy for the atomic jumping of  $(B_s - Si_i)$  pair. (Fit to the  $1/T_1$ data)

from the weighted mean of these results for three samples; to be

$$E_a = 0.47 \pm 0.04$$
 eV,  
 $\log_{10} \nu_0 = 9.4 \pm 0.5$  (in kHz). (5.4)

This obtained prefactor  $\nu_0 = 2.5 \times 10^{9}$  kHz of the jumping frequency is in agreement with a theoretical value of the effective attempt frequency ( $\sim 10^{10}$  kHz [MB93]) or the Debye frequency ( $\sim 8 \times 10^{10}$  kHz). The activation energy of 0.47 eV is comparable with the theoretical values of the migration energy for the interstitial Si of 0.5 eV [Has66], 0.4 eV [NVP89], or the sum of the Si interstitial migration energy of 0.5 eV and the extra Coulomb energy of 0.07 eV [Tar91]. These values will be taken up again in section 5.4.

Through ESR experiment, Watkins determined the jumping rate for the  $\langle 111 \rangle$  axial symmetry of the  $B^+$  defect as

 $\nu = 5 \times 10^9 \exp(-0.60 \pm 0.05 \text{ (eV)}/kT)$  (kHz).

This rate is shown in Fig.5.5 together with our present experimental rate. The present result shows slightly higher jumping rate compared with the ESR data, although the activation energies and the prefactors are in agreement. This slight deference may show a question in the identification of the sites between the one observed by Watkins [Wat75] and the one by us. This is an open problem in this stage.

We point out that an explanation for the steep decrease of the  $B_{ns}$  fraction suggested by Frank et al. who made similar  $\beta$ -NMR experiments is wrong [FDE<sup>+</sup>94]. They measured the temperature dependence of the amplitude of the resonance line at only the higher frequency  $\nu_L + \nu_{Qsplit}$  from the B<sub>ns</sub> nuclei. They found that the amplitude makes a

peak around 300 K. Their interpretation of the increase of the amplitude as the temperature is due to the direction change of the (111) symmetry associated with the atomic jump, which is correct. As for the steep decrease of the amplitude with the temperature, however, their interpretation is wrong. They explained it by a matter of rf applying technique, *i.e.*, lack of effective rf-applying time compared with a mean residence time  $\tau_c$ , which becomes shorter as temperature rises. As was made clear in the present study, the diminishing of the maintained polarization in this temperature range is due to the fast spin-lattice relaxation time, not the matter of rf applying technique.

#### Recovery of maintained polarization 5.3

In this section we will discuss the increasing of the maintained polarization in the temperature range of 450 K  $\sim$  550 K, which was described in the previous chapter.

The experimental results (Fig.4.1, 4.2) shows that all of the polarization produced by the nuclear reaction was fully maintained at the temperature below 275 K and above 550 K. In the intermediate temperature it shows constant quenched polarization ( $\sim$ 50 % of the reaction polarization). As discussed in the previous section the steep polarization change of it around 300 K is due to the fast  $T_1$  for the  $B_{ns}$  component associated with the atomic jumps. It is natural to suppose that the increasing polarization at the temperature above 450 K could be due to the vanishing of the cause of this spin-lattice relaxation. Added to it, the recovered polarization is emerged not in the B<sub>ns</sub> site but in the B<sub>s</sub> or the  $B_x$  sites.

The discussion will be made based on the assumption of the  $(B_s-Si_i)$  pair model, too. The followings seem to be possible cause of this recovery;

- averaging by the rapid atomic motion;
- (2) the dissociation of the the  $(B_s-Si_i)$  pair.

From the following reason, the motional averaging [(1)] may not be the cause of this recovery. When the frequency of the fluctuation is higher than the Larmor frequency, the relaxation time due to the fluctuating field becomes longer in inverse proportion to the correlation time  $\tau_c$ , because the destructive Fourier component of the rf field at the Larmor frequency is reduced. So the polarization could be recovered when the motion of the (B<sub>s</sub>-Si<sub>i</sub>) pair are extremely rapid compared with the Larmor frequency. In this case, because the averaging of the field leads to the narrowing of the resonance line, *i.e.*, the

(1) the vanishing of the quadrupole effect and the relaxation due to the motional

5.4. ON THE LATTICE LOCATION OF B<sub>NS</sub>

resonance will no longer show eqQ split lines but appear around the Larmor frequency. This mechanism, if it works, is simple, because the steep decrease and the recovery could both be explained by a single mechanism.

Solid and dotted lines in Fig.5.6 show the polarization change and the relaxation rate  $1/T_1$  using the present value of the  $E_a$  and the  $\nu_0$  determined from analysis of the steep decrease of  $B_{ns}$  polarization. This shows that the recovery of the polarization will be observed above  $\sim 1000$  K, which contradicts the present observation. Consequently, we reject this motional averaging mechanism for the recovery.

Idea of the dissociation of the  $(B_s-Si_i)$  pair is quite natural, because the dissociation of the pair leave the substitutional B alone separated from the interstitial Si. Resultant substitutional B naturally shows a resonance at the Larmor frequency if its nuclear polarization still be maintained.

In the following, this dissociation process will be treated quantitatively based on the (B<sub>s</sub>-Si<sub>i</sub>) pair model. The measured polarization change are fitted to a function considering the thermally induced dissociation rate  $\nu_r = \nu_{r0} \exp(-E_r/kT)$  and relaxation of the polarization induced by the atomic jump in the (B<sub>s</sub>-Si<sub>i</sub>) pair as was made clear in the previous section. The explicit form of the function is described in APPENDIX C. The fitting results are listed in Table 5.3. Though, it was unable to fit the data for the sample no.2 because of the lack of the data at higher temperatures. The difference of the fitting parameters depending on the type and density of the dopant was not seen within the error. So, we determine the activation energy  $E_r$  and the prefactor  $\nu_{r0}$  from the average of these data as

$$E_r = 0.84 \pm 0.06$$
 eV,  
 $\log_{10} \nu_{r0} = 9.7 \pm 0.5$  (in kHz). (5.5)

As seen in Fig5.7, these parameters well produces the experimental results.

Based on the above mentioned discussion, the outline on the polarization change can be illustrated as follows. Fig.5.8 shows the deduced dissociation rate and the jumping rate of the  $(B_s-Si_i)$  pair, and the relaxation rate due to the jumping. Below 275 K, full of the reaction polarization is observed because the relaxation rate due to the jumping are slow compared with the time scale of the nuclear lifetime and hence the  $\beta$ -NMR detection. Above the temperature, the relaxation rate becomes faster and the observed polarization for B<sub>ns</sub> becomes smaller as the temperature rise, resulting in also the decrease of the total detected polarization. At 325 K, the polarization of B<sub>ns</sub> totally vanishes. From the temperature up to 450 K, the  $B_{ns}$  is not detected. At 450 K, the dissociation rate of the (B<sub>s</sub>-Si<sub>i</sub>) pair becomes comparable with the relaxation rate, and the fractions of Table 5.3 Activation energy for the dissociation of  $(B_s - Si_i)$  pair.

			Logarithm of	
		Activation	pre-exponent	
Sample	Dopant	energy	factor	$\chi^2$ –Value
number	$(cm^{-3})$	Er(eV)	$\log_{10}(\nu_{r0}  (\rm kHz))$	(normalized)
1	$3\times 10^{14}~{\rm B}$	$0.80\pm0.08$	$9.5 \pm 0.6$	10.2
3	$6 \times 10^{14} \text{ P}$	$0.88 \pm 0.12$	$9.9\pm0.7$	5.4

 $B_s$  and  $B_r$  grow. Above 550 K, the dissociation rate completely overcome the relaxation rate and then all of the reaction polarization is detected as the B<sub>s</sub> and/or B<sub>x</sub>. Thus, the temperature dependence of the maintained polarization is explained convincingly. It is noted that through out the present temperature range, almost all the <sup>12</sup>B implanted in Si, regardless the type and density of the dopant, is suggested to be in diamagnetic states which can be detected by the  $\beta$ -NMR technique, since the total polarization detected is supposed to be close to that in Pt sample all the time.

### 5.4 On the lattice location of B<sub>ns</sub>

As described before, the deduced prefactors of the  $B_{ns}$  jump rate (eq.(5.4)) and the  $(B_s-Si_i)$  pair dissociation rate (eq.(5.5)) are both reasonable value, as they are of the order of 10<sup>9</sup> kHz which coincides with the order of lattice vibration frequency.

The activation energies of the  $B_{ns}$  jump and the the  $(B_s-Si_i)$  pair dissociation are listed in Table 5.4 together with the theoretical values of migrations of the self-interstitial and impurities which form defects in Si. The deduced activation energy of the jump is in agreement with the one that was deduced by ESR study within the experimental errors. And the activation energy of about 0.5 eV is almost the same with the theoretical values for the migration energy of the self-interstitial Si. Thus, the atomic jump and the polarization relaxation of  $B_{ns}$  can be understood by the migration of interstitial Si around the substitutional B in the  $(B_s-Si_i)$  pair model.

The activation energy of the dissociation of  $(B_s-Si_i)$  pair shows a slight difference with the one obtained by the Watkins' ESR measurement [Wat75], though the experimental errors of the ESR measurement was not shown. Tarnow gave the lower bound on the barrier of 0.54 eV which is the total energy difference between the initial and final configuration [Tar91]. Also he gave the Coulomb energy of 1.2 eV which is required for the Si atom to leave the (B<sub>s</sub>-Si<sub>i</sub>) pair alone. Our activation energy of 0.84 eV for the dissociation is an intermediate value between these two limit, to support the present  $(B_s-Si_i)$  pair model.

From what has been said, the behavior of the B<sub>ns</sub> atom and the temperature dependence of the nuclear polarization is well explained by the (B<sub>s</sub>-Si<sub>i</sub>) pair model. Although, the present experiment can't exclude the other configuration of the  $B_{ns}$  definitely, however, following two points are conclusive;

- the  $B_{ns}$  atom migrates between the four identical sites with the rate of  $\nu \sim 2.5 \times$  $10^9 \exp(0.47 \text{eV}/kT)$  kHz as deduced in section 5.2,
- the B<sub>ns</sub> defect dissociates with the rate of  $\nu_r \sim 5.0 \times 10^9 \exp(0.84 \text{eV}/kT)$  kHz as deduced in section 5.3.

Now, the other candidates for the B<sub>ns</sub> configuration are considered. Watkins suggested three probable configurations for this B defect [Wat75]; the bond centered site, the interstitial B - substitutional Si pair with slight compression along the (111) axis, and the hexahedral site.

When the B atom jumps into a Si-Si bond center, the bond should be broken by the B atom. Hence, the activation energy of the jump will be at least the binding energy of the bond, which is about 1.8 eV [Gil80]. Since the present obtained activation energy is too small to break the bond, the bond centered site is unrealistic.

If the other configurations, the interstitial boron or the hexahedral boron, are formed, the migration of the interstitial B will go through the interstitial of the lattice. Since the activation energy of 0.5 eV is typical value for the migration between interstitials as shown in Table 5.4, it cannot reject these configurations cannot be rejected in terms of the activation energy. In these configuration, the recovery of the polarization at higher temperature may be understood by the combination of the interstitial boron and the vacancy.

Of course, the most probable configuration is the  $(B_s-Si_i)$  pair as mentioned above, because Tarnow's calculation shows that (Bs-Sii) pair is more stable than the interstitial boron, channeling experiments also denied the undistorted tetrahedral interstitial B, and no reliable microscopic evidence for it has been reported so far.

It may be worth mentioning that ESR studies in aluminum-doped Si had demonstrated that the interstitial aluminum produced by electron irradiation at 20.4 K settles at the undistorted tetrahedral interstitial site and is stable to above 500 K [BL83]. This has been interpreted that the interstitial silicon atom, produced in the primary event, is mobile and kicks the substitutional aluminum atom into the interstitial site. Although 5.4. ON THE LATTICE LOCATION OF BNS

	Experimental $E_a$ (eV)	Theoretical $E_a$ (eV)
Jumping (reorientation) of $B_{ns}$ atom	$0.47 \pm 0.8$ (present) $0.60 \pm 0.5$ [Wat75]	0.5 [Tar91]
Discontinue of the D. defect	$0.84 \pm 0.06$ (present)	> 0.54 [Tar91]
Dissociation of the B <sub>ns</sub> defect	0.6 [Wat75]	(1.2 * [Tar91])
C: Interstitial		0.5 [Has66]
Si Interstitiai		0.4 [NVP89]
		1.1 [Has66]
Si – Vacancy	-	0.3 [NVP89]
		0.7 [D+76]
B interstitial	-	0 [NVP89]
B – Vacancy	-	1.0 [NVP89]
P interstitial	-	0.8 [NVP89]
P – Vacancy	0.94 [HHS69]	
As interstitial	-	0.4 [NVP89]
As – Vacancy	1.07 [HHS69]	-
Sb interstitial	-	0.2 [NVP89]
Sb – Vacancy	1.28 [HHS69]	-

\* The Coulomb energy required for the Si atom to leave alone.

boron and aluminum are the same group-III elements, B prefers forming (B<sub>s</sub>-Si<sub>i</sub>) pair, while Al prefers (Al<sub>i</sub>-Si<sub>s</sub>) pair. This is an interesting issue to be solved.

Up to here we discussed about the polarization change of B<sub>ns</sub> nuclei, we obtain another important information of the electric field gradient q of it. The  $|q(B_{ns})|$  is  $(1.14\pm0.04)\times10^{17}$  V/cm<sup>2</sup>, and  $\eta=0.0$ . The ESR measurements obtained the  $|q(B^-)|$  of the  $(1.02\pm0.04)\times10^{17}$  V/cm<sup>2</sup>, and  $\eta=0.18\pm0.05$  [Wat75]. To make sure the configuration of B<sub>ns</sub>, a theoretical calculation for these field gradients are planned. In APPENDIX B, the electric field gradients of other defects related with impurity are listed.

CHAPTER 5. DISCUSSIONS

#### On the broad resonance from $B_X$ nuclei 5.5

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It was disclosed that the broad resonance ( $\sim 10$  kHz) from  $B_x$  site is due to static quadrupole interactions with no special symmetry. The fraction of  $B_x$  decreases as increasing temperature. From these results, the most probable site for the  $B_x$  component is also the substitutional site with small electric field gradient due to crystal defects like vacancies. However, the detail of the character and the cause of this defect need further advanced investigation.





(c) Si Lattice



Figure 5.1 Proposed metastable atomic configurations [Tar91] (a) for positive charge state  $B^+$  in Si, which is almost at the substitutional site combined with an interstitial Si, (b) for neutral and negative charge states. (c) Si lattice (just for a reference).

(b) Configuration for  $B^0$  and  $B^-$ .



Interatomic distance

(B <sup>0</sup> )	(B <sup>-</sup> )
d1 = 2.03 Å	d1 = 2.05 Å
d2 = 2.01  Å	d2 = 2.01  Å
d3 = 2.20 Å	d3 = 2.12  Å
d4 = 2.35 Å	d4 = 2.31  Å

Lattice constant a = 5.43 Å  $\left(\frac{\sqrt{3}}{4}a = 2.35\text{\AA}\right)$ 









Figure 5.3 The effect of the spin-lattice relaxation time  $T_1$  in p-type Si  $(7 \times 10^{17})$  $B/cm^3$ ). (a) The best fit line to the observed polarization change within the counting time of 40 ms. (b) The solid line shows the calculated  $1/T_1$ as a function of temperature using the activation energy and the prefactor obtained from the fitting of (a). The dotted line is the best fit line to the data of the  $1/T_1$  (closed circles) which was deduced in the section 4.4.1.







Figure 5.5 The solid line shows the determined jumping rate as a function of

temperature  $\nu = 2.5 \times 10^9 \exp(-0.47 (\text{eV})/kT)$  kHz. The dotted line is the reorientation rate determined by Watkins [Wat75].







Figure 5.7 The best fit lines to the observed polarization change on the astermined in the section 5.1.

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sumption of  $(B_s-Si_i)$  pair dissociation. The fitting region is above 320 K. The lines below 320 K are calculated using the values de-



Figure 5.8 The deduced dissociation rate of the (B<sub>s</sub>-Si<sub>i</sub>) pair and the deduced jumping rate of it. The dotted line shows the relaxation rate due to the jump. In present  $\beta$ -NMR experiment, the <sup>12</sup>B can be observed only when the  $1/T_1$  is below about 10 ms. The dashed line is, just for a reference, the migration rate deduced from the self-diffusion coefficient of silicon [S<sup>+</sup>86] on the assumption that Si diffuses with the interstitial mechanism and that its activation energy equals the migration energy itself.

# Chapter 6

### Summary

We have studied the behavior of the B atom implanted in Si, using a probe nuclei <sup>12</sup>B by means of the  $\beta$ -NMR technique, especially on the locations of the <sup>12</sup>B recoil implanted in Si crystal. We determined the fractions of three locations in the temperature range from 100 K to 800 K.

In addition to the previously known sites, *i.e.*, the substitutional site  $(B_s)$  and the nonsubstitutional site  $(B_{ns})$  with  $\langle 111 \rangle$  axial symmetry, a broad resonance was found around the Larmor frequency for the first time. This corresponds to the 'missing fraction' in the previous studies, and all implanted B atom are observed by NMR. Actually it was found that almost all the <sup>12</sup>B are located in their diamagnetic states.

We determined the fraction of each component without uncertainty. The results (Fig.4.18-4.20) of these fractions are as follows.

- (1) The fraction of the  $B_{ns}$  atom is constant (~35 %) below 260 K.
- disappears at the temperatures higher than 325 K.
- about 40 %.
- %.

It is disclosed that the steep decrease of  $B_{ns}$  fraction is caused by a thermal jump of the B<sub>ns</sub> atom between the identical locations, *i.e.*, the fluctuating electric field gradient due to the thermal jump causes the fast spin-lattice relaxation of the nuclear polarization of  ${}^{12}B$  in  $B_{ns}$  sites. Assuming the Arrhenius behavior of the thermal jump, the jump rate of the  $B_{ns}$  was deduced based on the  $(B_{s}$ -  $Si_{i})$  pair model for the atomic configuration

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(2) At 260 K and above, the fraction of the  $B_{ns}$  component rapidly decreases and

(3) The sum of the fractions of  $B_s$  and  $B_x$  is constant (~ 65 %) from 100 K to 450 K. In this temperature range the  $B_s$  fraction increases monotonically from few % to

(4) Above 450 K, the sum of the fractions  $(B_s + B_x)$  is increases rapidly and reaches to 100 % at the temperature of 550 K. The B<sub>s</sub> fraction also increases to about 80

which was predicted theoretically to be most probable. The obtained jumping rate is  $(2.5 \times 10^9) \exp(-0.47 \pm 0.04 (eV)/kT)$  kHz ( the error of the pre-exponential factor is  $+6 \times 10^9$ ,  $-1.5 \times 10^9$ ). As well as the decrease of the B<sub>ns</sub> fraction, the recovery of the <sup>12</sup>B fraction in the B<sub>s</sub> site or the B<sub>x</sub> site above 450 K is successfully understood by the dissociation of (B<sub>s</sub>- Si<sub>i</sub>) pair with the dissociation rate of  $5 \times 10^9 \exp(-0.84 \pm 0.06 (eV)/kT)$  kHz ( the error of the pre-exponential factor is  $+1.1 \times 10^{10}$ ,  $-3.5 \times 10^9$ ).

Thus the steep decrease of  $B_{ns}$  fraction above 260 K and the polarization recovery around 500 K are consistently explained by the thermal jump and the dissociation within the ( $B_{s}$ - Si<sub>i</sub>) pair model.

The electric field gradient q at the  $B_{ns}$  site was precisely determined to be  $1.14 \pm 0.04 \times 10^{17} \text{ V/cm}^2$ . In order to make sure the atomic configuration for  $B_{ns}$  site, a theoretical calculation based on the KKR method for the energy minimum configuration and for the field gradient is planned.

A new broad resonance line from the  $B_x$  site was found to have the two features; (1) a static quadrupole interaction makes the resonance broad, (2) the quadrupole field has no special symmetry axis. As a consequence of these, the most probable site for the  $B_x$  component is supposed to be also the substitutional site with small electric field gradient due to crystal defects like vacancies. To clarify what interaction is accompanied with the  $B_x$  atom, the cause of this defect should be investigated.

### Future prospect

Although it is revealed that the spin-lattice relaxation is caused by the atomic jump of  $B_{ns}$ , the lifetime of a probe nuclei restricts the time window for the measurement to several tens milli-second. The  ${}^{8}B(T_{1/2}=760 \text{ ms}, I^{\pi}=2^{+})$  nuclei is available to measure the relaxation phenomena in the longer time window than the present case of the  ${}^{12}B$ . The long lifetime of  ${}^{8}B$  is expected to help to study the atomic jump at higher temperatures.

As the the relaxation time is determined by the relation between the mean residence time and the Larmor frequency, the relaxation time will be changed in accordance with the Larmor frequency which can be controlled by the external magnetic field. That is the  $\beta$ -NMR measurements at different external magnetic fields should be helpful.

As the crystal has four equivalent  $\langle 111 \rangle$  axis;  $\langle 111 \rangle$ ,  $\langle \bar{1}11 \rangle$ ,  $\langle 1\bar{1}1 \rangle$ , and  $\langle \bar{1}\bar{1}1 \rangle$ , the partial destruction, *e.g.*, the polarization destruction of the B<sub>ns</sub> nuclei with  $\langle 1\bar{1}1 \rangle$  axial symmetry,

the  $B_{ns}$  atomic jump can be directly observed as the polarization change in another site with different symmetry. So the experiment with different crystal orientation may be helpful for the clear understanding of the thermal jump for  $B_{ns}$ .

In summary, we detected for the first time all the diamagnetic states of the implanted B and revealed a dynamic behavior of the boron related defects. In order for the better understanding of the behavior of B in Si, we extend the present  $\beta$ -NMR study in many directions.

# Appendix A NMR

### A.1 Magnetic interaction

The motion of the magnetic moment in a magnetic field can be described by the classical dynamics as follows.

A magnetic moment  $\mu$  in a static magnetic field  $H_0$  receives the torque  $\mu \times H_0$ . This magnetic interaction leads to the precession of  $\mu$  around the direction of  $H_0$ with a frequency  $\nu_L = \gamma H_0/2\pi$  (Larmor frequency), where the gyromagnetic ratio  $\gamma$  is the ratio of the  $\mu$  and the angular moment  $I\hbar$ . Defining z-axis is along the direction of  $H_0$ , additional rotating magnetic field  $H_1(t)$  is supposed to be applied, *i.e.*,

### $\boldsymbol{H}_{1}(t) = H_{1}(\boldsymbol{i})$

The Hamiltonian of the magnetic moment  $\mu = \gamma \hbar I$  is

 $\mathcal{H} =$ 

The eigenstates of this Hamiltonian are split into 2I + 1 levels (Zeeman splitting) with energies;

$$E_m = -\gamma \hbar H_0 m$$

They are illustrated in Fig.A.2 for the case of I = 1, as is in the case of <sup>12</sup>B. These energy levels are equally separated with the energy gap of  $h\nu_L$ .

$$\cos\omega t + \boldsymbol{j}\,\sin\omega t) \tag{A.1}$$

perpendicular to  $H_0$ . In a rotating frame fixed to the rotating field with an angular frequency of  $\omega$ , the magnetic moment rotates around the effective magnetic field  $H_{eff} =$  $k (H_0 + \omega/\gamma) + i' H_1$  (Fig.A.1). When  $\omega$  is equal to  $-\gamma H_0$ , the effective field is just  $H_1$  as shown in Fig.A.1, and the moment will precess around it. As a results, the time averaged expectation value of the magnetic moment along the z-direction becomes zero. This resonance phenomena can be also understood as follows quantum mechanically.

$$-\boldsymbol{\mu} \cdot \boldsymbol{H}_0$$
$$-\gamma \hbar H_0 \boldsymbol{I}_z. \tag{A.2}$$

$$m = I, I - 1, \cdots, -I. \tag{A.3}$$

APPENDIX A. NMR

The transitions between the relevant levels are induced by the rotating magnetic field  $H_1(t)$  (Eq. A.1). If the rotating field can be treated as a perturbation  $\mathcal{H}_1 = -\gamma \hbar H_1 \cdot I$ , the transition probability between magnetic substates m and m + 1 is given as

$$W_{m+1,m} = \frac{2\pi}{\hbar} |\langle m | \mathcal{H}_1 | m+1 \rangle|^2 \delta(E_m - E_{m+1} - \hbar \omega_L) = \frac{\pi \hbar}{2} \omega_1^2 \left\{ I(I+1) - m^2 - m \right\} \delta(E_m - E_{m+1} - \hbar \omega_L),$$
(A.4)

where  $\omega_1 = -\gamma H_1$ . Therefore, when the rotating field with the Larmor frequency is applied to the spins, the probabilities of occupation of both states are equalized.

In a actual experiment, the energy levels spread around the central values, due to spread of the local field originated from the nuclear spin-spin interaction. Therefore, the  $\delta$ -function in Eq.A.4 has to be replaced by the line shape function  $f(\hbar\omega)$ .

#### Electric quadrupole interaction A.2

In an electric field gradient, a nucleus with the quadrupole moment Q interacts with it in addition to the magnetic interaction. The  $3 \times 3$  tensor of the electric field gradient, which is the second derivative of the electrostatic potential V(r), can be simplified by selecting a principal axes in good symmetries so that off-diagonal components vanishes:  $V_{ij} = 0$  for  $i \neq j$ . Then the Hamiltonian of the electric quadrupole interaction is given as

$$H_Q = \frac{eQ}{4I(2I-1)} \left[ V_{ZZ} (3I_Z^2 - I^2 + \frac{1}{2}(V_{XX} - V_{YY})(I_+^2 + I_-^2) \right]$$
(A.5)

$$\frac{eqQ}{4I(2I-1)} [3I_Z^2 - I^2 + \frac{\eta}{2}(I_+^2 + I_-^2)].$$
(A.6)

Here, the asymmetry parameter  $\eta$  and the largest component of the field gradient q are defined as

$$eq = V_{ZZ} \tag{A.7}$$

$$\gamma = \frac{V_{XX} - V_{YY}}{V_{ZZ}} \tag{A.8}$$

$$|V_{XX}| \le |V_{YY}| \le |V_{ZZ}| \,. \tag{A.9}$$

In the present study where high field  $H_0$  was employed, this quadrupole interaction can be treated as a perturbation to the magnetic interaction, since  $eqQ \ll \mu H_0$ . In order to derive the perturbation energies, the perturbation Hamiltonian  $H_Q$  is expressed in the coordinate system with the z axis parallel to  $H_0$ . Using the Euler angles defined in Fig.A.3:

$$\begin{split} H_{Q} &= \frac{h\nu_{Q}}{4} \left[ \left\{ I_{z}^{2} - \frac{1}{3}I\left(I+1\right) \right\} \left\{ 3\cos^{2}\theta - 1 + \eta\cos2\phi\sin^{2}\theta \right\} \\ &+ \left( \frac{1}{2}\sin2\theta - \frac{\eta}{6}\cos2\phi\sin2\theta + i\frac{\eta}{3}\sin2\phi\sin\theta \right) \left( I_{+}I_{z} + I_{z}I_{+} \right) \\ &+ \left( \frac{1}{2}\sin2\theta - \frac{\eta}{6}\cos2\phi\sin2\theta - i\frac{\eta}{3}\sin2\phi\sin\theta \right) \left( I_{-}I_{z} + I_{z}I_{-} \right) \\ &+ \left( \frac{1}{2}\sin^{2}\theta + \frac{\eta}{6}\cos2\phi\left(1 + \cos^{2}\theta\right) - i\frac{\eta}{3}\sin2\phi\cos\theta \right) I_{+}^{2} \\ &+ \left( \frac{1}{2}\sin^{2}\theta + \frac{\eta}{6}\cos2\phi\left(1 + \cos^{2}\theta\right) + i\frac{\eta}{3}\sin2\phi\cos\theta \right) I_{-}^{2} \right], \end{split}$$
(A.10)

where  $\nu_Q = \frac{3eqQ}{2I(2I-1)h}$  is the coupling frequency of the quadrupole interaction. By means substates are given as

$$E_{m} = E_{m}^{(0)} + E_{m}^{(1)} + E_{m}(2) + \cdots$$
(A.11)  

$$E_{m}^{(0)} = -h\nu_{L}m$$
(A.12)  

$$E_{m}^{(1)} = \frac{1}{4}h\nu_{Q}(3\cos^{2}\theta - 1 + \eta\cos 2\phi\sin^{2}\theta) \left(m^{2} - \frac{1}{3}I(I+1)\right)$$
(A.13)  

$$E_{m}^{(2)} = -\frac{h\nu_{Q}^{2}}{16\nu_{L}}m \left[2B\left(-2m^{2} + 2I(I+1) - 1\right)\right]$$

Here,

$$B = \left(\frac{3}{4}\sin^2\theta + \frac{\eta}{4}(\cos^2\theta + 1)\cos 2\phi\right)^2 + \left(\frac{\eta}{2}\cos\theta\sin 2\phi\right)^2$$
$$C = \left(\frac{3}{4}\sin 2\theta - \frac{\eta}{4}\sin 2\theta\cos 2\phi\right)^2 + \left(\frac{\eta}{2}\sin\theta\sin 2\phi\right)^2.$$
(A.15)

The effect of the quadrupole interaction is shown in Fig.A.4 for the case of a spin I = 1. The transition frequency between m and m + 1 is shifted by about  $\Delta E$  which is proportional to m from the Larmor frequency. As a consequence the 2I resonances lines are observed.

of the first and the second order perturbation theory, the energy levels of the magnetic

$$+2I(I+1) - 1) + C\left(8m^2 - 4I(I+1) + 1\right) ].$$
 (A.14)

### APPENDIX A. NMR



A magnetic moment precesses along the external magnetic field  $H_0$  with the Larmor frequency.  $(\omega_{\rm L} = -\gamma H_0)$ 



The effective magnetic field and the Larmor precession in the rotating frame fixed to the rotating field  $H_1$  with the angular velocity  $\omega$ .



The precession at the  $\omega = \omega_{\rm L}$ . The magnetic moment rotates in the y'z plane with the angular velocity  $\omega_1 = -\gamma H_1$ .

Figure A.1 The motion of a magnetic moment.



Figure A.2 The energy levels for I = 1 nuclear spin ensemble. The polarization is defined by  $P = \frac{\langle I_z \rangle}{I}$ .

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At the on resonance condition, the relevant transitions between the substates are induced, and all of the populations are equalized.

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(b)



Figure A.4 Energy and transition-frequency shifts for the case of I = 1 caused by the quadrupole effect in high field.

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$H_0$	≠0	
eq	) ≠ (	

$H_0$	≠0	
eq	) ≠ (	)

1st order perturbation 2nd order perturbation

# Appendix B Electric Field Gradients of defects in Si

In Table B.1, the electric field gradients for impurity-defects in Si observed experimentally are shown. Since the electric field gradients are affected by the nonspherical part of the electronic shell, this contributions are taken into account by replacing  $V_{zz}$  by  $V_{zz}/(1-\gamma_{\infty})$  (the Sternheimer effect ). The  $V_{zz}/(1-\gamma_{\infty})$  are in the range of 10<sup>16</sup> to 10<sup>18</sup>.



Defect	Probe	$V_{zz}~({ m V/cm^2})$	$V_{zz}/(1-\gamma_{\infty})$	Direction	Method	Reference
B(+)	<sup>12</sup> B	$1.1 \times 10^{17}$	$3.6  imes 10^{17}$	(111)	$\beta$ -NMR	Present
B(0)	<sup>11</sup> B	$1.0  imes 10^{17}$	$3.2 \times 10^{17}$	$\sim \langle 111 \rangle$	ESR(ENDOR)	[Wat75]
$B_s - Fe_i$	<sup>11</sup> B	$3.5 \times 10^{16}$	$1.1  imes 10^{17}$		ESR(ENDOR)	[GS83]
$\mathrm{Al}_{\mathrm{i}}-\mathrm{Al}_{\mathrm{s}}$	<sup>27</sup> Al	$4.8  imes 10^{16}$	$1.4 \times 10^{16}$	(111)	ESR(ENDOR)	[NSW85]
$F_{\rm i}-Si_{\rm s}$	<sup>19</sup> F	$1.3  imes 10^{18}$		$\langle 111 \rangle$	TDPAD	[SHM95]
$Mn_i - B_s$	<sup>55</sup> Mn	$4.4  imes 10^{17}$	$5.8 \times 10^{16}$	-	ESR(ENDOR)	[kG82]
$\rm In/Cd_s - As_s$	<sup>111</sup> Cd	$1.1 \times 10^{18}$	$3.5 \times 10^{16}$	-	PAC	[WDG+89]
$\rm In/Cd_s - Li_i$	<sup>111</sup> Cd	$1.2 \times 10^{18}$	$3.9 \times 10^{16}$	-	PAC	[DKP+89]
$\rm In/Cd_s-H_i$	<sup>111</sup> Cd	$2.2 \times 10^{18}$	$7.2 \times 10^{16}$		PAC	[WDG+89]
$\mathrm{Au}_{\mathrm{i}} - \mathrm{Si}$	<sup>197</sup> Au	$1.6 \times 10^{19}$	$4.2 \times 10^{17}$	al a spinor	ESR(ENDOR)	[Hoh86]

in the second se	
Probe	$(1-\gamma_{\infty}).$
В	0.32
Al	3.46
Mn	7.6
Cd	30.27
Au	39.14

.

Table B.1 Comparison of q.

Table B.2 Sternheimer antishielding factors for free atoms

## Appendix C

### **Fitting Functions**

In this section, we will describe the experimental fitting functions for the polarization relaxation due to fluctuating electric field gradients.

The general formula for the polarization relaxation rate were obtained as equations (2.35) and (2.36) in § 2.3.3. For the special case of spin I = 1 nuclei, the eq.(2.35) can be simplified as

$$\frac{1}{T_1} = \frac{(eqQ)^2}{8\hbar} \left\{ k_1(\omega_0) + 4k_2(2\omega_0) \right\}.$$
(2.37)

The correlation function  $k_q(\omega_q)$  depends on a specific model of the fluctuation. For the analysis of the present experimental results, the correlation function were calculated on the assumption of the  $(B_s - Si_i)$  pair model.

In this model, there are four identical sites corresponding to the four direction of the  $\langle 111 \rangle$  axes, *i.e.*,  $\langle 111 \rangle$ ,  $\langle \overline{1}11 \rangle$ ,  $\langle 1\overline{1}1 \rangle$ , and  $\langle \overline{1}\overline{1}1 \rangle$ . For the explanation, we label the site with (111) axial symmetry as A, in the same manner, B for  $(\overline{1}11)$ , C for  $(1\overline{1}1)$ , and D for  $(\overline{111})$ . The fluctuation is caused by the jumping of the Si<sub>i</sub> atom from a (111) axial symmetry site to other  $\langle 111 \rangle$  axial symmetry site through hexagonal interstitial sites. Therefore the atom jumps from A to B (or C, D), not from A to A.

Assuming each jump obeys the Poisson process with the mean occurrence of  $1/\bar{\tau}_c$ , the probability for n times of events in a period  $\tau$  represent as

$$w_n(\tau) = \frac{1}{n!} \left(\frac{\tau}{\tau_c}\right)^n e\left(-\frac{\tau}{\tau_c}\right).$$
(C.1)

Therefore, when the atom is in site A at t = 0, the probability for the atom to be in the same site A after  $t = \tau$  is

$$P_A(\tau) = \sum_{n=1}^{\infty} w_n(\tau) P_{A,n}.$$
 (C.2)

Here, the  $P_{A,n}$  is the probability that the atom is still in the same site A after n jumps, which is calculated in this case as

$$P_{A,n} = \frac{1}{4} \left[ 1 + 3 \left( -\frac{1}{3} \right)^n \right].$$
(C.3)

In the same manner, the probability for the atom to be in another site B at  $t = \tau$  is

$$P_B(\tau) = P_{B,n} =$$

Then we can calculate the correlation function for this case using eq.(2.38) as

$$k_1(\omega_0) =$$

 $k_2(2\omega_0) =$ 

Fitting Function for the jumping effect

The relaxation rate  $\Lambda$  due to the fluctuating field is,

$$\Lambda = \frac{1}{T_1}$$

$$= \frac{(eqQ)^2}{8\hbar^2} \{k_1(\omega_0) + 4k_2(2\omega_0)\} + K(\text{Constant}), \quad (C.6)$$

$$k_1(\omega_0) = \frac{1}{4} \frac{2\tau_c}{1 + \omega_0^2 \tau_c^2}, \quad (C.7)$$

$$k_2(2\omega_0) = \frac{5}{16} \frac{2\tau}{1 + 4\omega_0^2 \tau_c^2}, \quad (C.8)$$

$$\frac{1}{\tau_c} = \nu = \nu_0 \exp(-\frac{E_a}{kT}). \quad (C.9)$$

Here, the constant K in the relaxation rate  $\Lambda$  is for the contribution from the other cause than the preset fluctuating electric field gradient. This is a fitting function used in the analysis of the polarization relaxation.

For the calculation of the actually observed average polarization change in the  $\beta$ -ray counting period, the correction due to the relaxation is necessary for the actual timing program of the  $\beta$ -NMR detection. Thus, the observed polarization is given as

$$\Delta P = \frac{P_0 \lambda^2 (1 - e^{-(\Lambda + \lambda)t_1}) (1 - e^{-(\Lambda + \lambda)t}) e^{-\Lambda t_2}}{(\Lambda + \lambda)^2 (1 - e^{-\lambda t_1}) (1 - e^{-\lambda t})},$$
(C.10)

where  $\Lambda$  is the polarization relaxation rate,  $\lambda$  is the nuclear decay rate,  $P_0$  is the initial polarization at the production time,  $t_1$  is the beam bombardment time,  $t_2$  is the rf time, and t is counting time.

$$\sum_{n=1}^{\infty} w_n(\tau) P_{B,n},$$
(C.4)
$$\frac{1}{4} \left[ 1 - \left( -\frac{1}{3} \right)^n \right].$$
(C.5)

$$\frac{1}{4} \frac{2\tau}{1 + \omega_0^2 \tau_c^2},\tag{2.41}$$

$$\frac{5}{16} \frac{2\tau}{1 + 4\omega_0^2 \tau_c^2}.$$
(2.42)

Fitting Function for the dissociation of (B<sub>s</sub> - Si<sub>i</sub>) pair

For the analysis of the dissociation of  $(B_{s}$ -  $Si_{i})$  pair, different correction is necessary because the polarization is kept after the dissociation. So, the function for average polarization taking into account of the dissociation rate  $\nu_r$  is given as

$$\Delta P = \frac{P_0 \lambda^2 \Lambda (1 - e^{-(\Lambda + \lambda + \nu_r)t_1}) (1 - e^{-(\Lambda + \lambda + \nu_r)t}) e^{-(\Lambda + \lambda)t_2}}{(\Lambda + \lambda + \nu_r)^2 (\Lambda + \lambda) (1 - e^{-\lambda t_1}) (1 - e^{-\lambda t}) e^{-\lambda t_2}} + \frac{\nu_r}{\Lambda + \nu_r}, \tag{C.11}$$

where,  $\nu_r$  is the dissociation rate of (B<sub>s</sub>-Si<sub>i</sub>) pair,  $\nu_r = \nu_{r0} e(-E_r/kT)$ .  $E_r$  is the activation energy and  $\nu_{r0}$  is the prefactor of the thermal dissociation, the rest of the symbols are same as used in eq.(C.10).

# Appendix D Computer control program lists

We list computer programs for  $\beta$ -NMR and  $\beta$ -NQR method. These program are written by machine language MASM (macro assembler) for the 80286 CPU. They contain two part, main programs and macro libraries.

File Name 2APCNTRF.ASM LIFCNTR.ASM LAB1CNTR.ASM LAB2CNTR.ASM IOCNTR.ASM

Table D.1 List of computer programs

Experimental mode β-NMR 2APCNTRZ.ASM  $\beta$ -NQR (5 rf repetitions) 2APCNTRI.ASM  $\beta$ -NQR (1 rf repetition) Time spectrum macro library macro library macro library

2APCNTRF.ASM NMR 測定実験制御 2AP MODE 2APCNTRF.M for ca .sall title 2APCNTRF Main routine %out Now 2APCNTRF.ASM has been compiled 初期設定部インクルード include "lab"lablcntr.asm ctadinc 3Ch bpcntr bmport,bmstart,off,lpulse rfdtout adrfdt wtloopl bmtimel,bmtime2 bpcntr bmport,bmstop,off,lpulse in sem adctsem, ctch5 bmcool rfcntr rfon,rfoff,rftime1,rftime2 count 00000001b,01h,04h,cttime3,cttime4 countin count 10000001b.01h.04h.cttime3.cttime4 count 00000010b,01h,04h,cttime3,cttime4 10000010b.01h.04h.cttime3.cttime4 count 00010000b,01h,04h,cttime3,cttime4 count 01010000b,01h,04h,cttime3,cttime4 10010000b,01h,04h,cttime3,cttime4 ount 11010000b,01h,04h,cttime3,cttime4 ount 00000100b,01h,04h,cttime1,cttime2 countin count\_10000100b,01h,04h,cttime1,cttime2 00001000b,01h,04h,cttime1,cttime2 ount 10001000b,01h,04h,cttime1.cttime2 count\_00100000b,01h,04h,cttime1,cttime2 countin count 01100000b,01h,04h,cttime1,cttime2 countin count 10100000b,01h,04h,cttime1,cttime2 count\_11100000b,01h,04h,cttime1,cttime2 rfadinc bpcntr ctport,workend,off,lpulse dec jcxz jmp cx extgl mair extgl 終了処理部インクルード

include "lab"lab2cntr.asm end

### 2APCNTRZ.ASM

#### NMR測定実験制御

2RF 2AP MODE (RF ON / OFF) RF 1,2 \* 5 (3,4 are dummy) used by Frequency synsesizer

2RF-2AP using frequency synsesizer

RF data for '4RF 2AP MODE' can be used Please set dummy data for No. 3 and 4 RF. 2APCNTRZ.M

by Moichi

modified by A.K. 1991/11/08 This is the my Last for LABCNTR system.

for camac scaler title 2APCNTRZ Main routine if1 %out Now 2APCNTRZ.ASM has been compiled endif

初期設定部インクルード

include lab"lab1cntr.asm

ctadinc 04h. bpcntr bmport,bmstart,off,lpulse wtloopl bmtime1,bmtime2 bpcntr bmport,bmstop,off,lpulse in sem adctsem,ctch5 bmcool bpcntr rfport, rfon, rfon, lpulse push cx cx,005h ; for 5 rf loop mov cx,005h ; tor s rflp1: push cx rfdtout adrfdt bpcntr rfport,045h,004h,1pulse ; select RG1 0100 0101 wtloop1 rftime1,rftime2 rfadinc rfdtout adrfdt bpcntr rfport,025h,004h,lpulse ; select RG2 0010 0101 wtloopl rftime1,rftime2 rfadinc rfadinc pop cx dec cx jcxz cont1 rfaddec3 jmp rflp1 cont1: pop cx bpcntr rfport,rfoff,rfoff,lpulse rfkill count 00000001b,01h,3ch,cttimel,cttime2 count 00000001b,01h,40h,cttime1,cttime2 countin rfadinc dec cx jcxz extgl jmp main extgl: 終了処理部インクルード

include lab"lab2cntr.asm end

### 2APCNTRI.ASM

#### NMR測定実験制御

2RF 2AP MODE (RF ON) 16sections RF 1,2 (3,4 are dummy) used by Frequency synsesizer 2RF-2AP using frequency synsesizer

RF data for '4RF 2AP MODE' can be used Please set dummy data for No. 3 and 4 RF 2APCNTRI.M

by Moichi

modified by A.K. 1991/11/08 This is the my Last control program for LABCNTR system. modified by Miyake. '93 X'mas Eve modified by Miyake. '94 / 06/ 11

for camac scaler 94/11/25 title 2APCNTRI Main routine

if1 %out Now 2APCNTRI.ASM has been compiled endif

- 初期設定部インクルード
- include lab"lab1cntr.asm

ctadinc 3Ch

st'sem

bpcntr bmport,bmstart,off,lpulse wtloopl bmtimel,bmtime2 bpcntr bmport,bmstop,off,lpulse in sem adctsem,ctch5

bmcool

i bpcntr rfport.rfon.rfon.lpulse rfdtout adrfdt bpcntr rfport.045h.004h.lpulse ; select RG1 0100 0101 wtloopl rftime1.rftime2 rfadinc

### rfdtout adrfdt bpcntr rfport,025h,004h,1pulse ; select RG2 0010 0101 wtloopl rftime1,rftime2 rfadinc rfadinc

bpcntr rfport,rfoff,rfoff,lpulse rfkill

count 00000001b,01h,04h,cttime1,cttime2 00000010b,01h,04h,cttime1,cttime2 count 00000011b,01h,04h,cttime1,cttime2 count 00000100b,01h,04h,cttime1,cttime2 countir count 00000101b,01h,04h,cttime1,cttime2 00000110b,01h,04h,cttime1,cttime2 00000111b,01h,04h,cttime1,cttime2 count count 00001000b,01h,04h,cttime1,cttime2 00001001b,01h,04h,cttime3,cttime4 count 00001010b,01h,04h,cttime3,cttime4 00001011b.01b.04b.cttime3 cttime4 ount 00001100b,01h,04h,cttime3,cttime4 count 00001101b,01h,04h,cttime3,cttime4 00001110b,01h,04h,cttime3,cttime4 n 00001111b,01h,04h,cttime3,cttime4 count countin count 00010000b,01h,04h,cttime3,cttime4 rfadinc

cx extgl main jcxz jmp extgl:

> 終了処理部インクルード include lab"lab2cntr.asm end

### LIFCNTR.ASM

NMR测定実験制御 life time

LIFCNTR .M

1994/11/30 BEAM \* 2ch by T.M 1994/11/30 to use CAMAC by T.M

title LIFCNTR Main routine if1 %out Now LIFCNTR .ASM has been compiled endit

初期設定部インクルード

include lab"lab1cntr.asm

st'beam st'beam bpcntr bmport,bmstart,off,lpulse ridtout adridt wtloopl bmtimel,bmtime2 bpcntr bmport,bmstop.off,lpulse in beam adctsem,ctch5,ctch6

bmcool

cloop count 00010000b,01h,40h,cttime1,cttime2 countin

> dec jcxz jmp cx extgl cloor

extgl: bpcntr ctport,workend,off,lpulse

終了処理部インクルード

include lab"lab2cntr.asm

### LAB1CNTR.ASM

実験創御プログラム 初期設定ルーチン for controller NEC PC9801VX

1991/01/25 by A.Kitagawa 1994.01.25 to use WAVETEK modified by T.Miyake 1994.11.30 to use CAMAC modified by T.M 1995.10.12 modified WAVETEK control

%out LABCNTR v.11.10 1.01 endif if2

%out path2

endif

インターフェイス ボートアドレス 01ad0h

inport equ bmport equ rfport equ ptlctr equ rfbitpl equ rfbitph equ secport equ pt2ctr equ 01ad0h 01ad4h 01ad2h 01ad4h 01ad6h 01ad8h 01adah 01adch 01adeh synthe equ 20d4h synt01 equ 020d2h synt10 equ 020dch synt1k equ 020dah synt100k equ 020d8h synt10m equ 020d0 syntstr equ 020d4h 020d0h SCALLER1 equ 8 SCALLER2 equ 8

open equ Offh hold equ O0h rddt equ Oh

datalow equ 0D0h datahi equ 0D2h nacmnd equ 0D4h contrl equ 0D6h camacgo equ 0D7h status equ 0D6h ; camac controll bit

c'line equ 00000001b i'line equ 00000100b done equ 0001000b lint'ei'i equ 10001100 lint'ei equ 10001000b

ctch1 equ ctch2 equ ctch3 equ ctch4 equ ctch5 equ ctch6 equ 0h 1h 2h 3h 4h 5h

データアドレスオフセット adnrf equ adrfdt equ 900h 904h adctul equ adctdl equ adctu2 equ adctd2 equ 908h 90ch 910h 914h

adctsem equ 918h adwtlp equ adnlp equ 91ch 920h adwork equ 924h aderror equ 91ch ; エラーフラグ (待時間データの先頭) 引数受渡し

nparal equ 12h npara2 equ 10h npara3 equ 24h WAITデータ オフセット dummyt equ 0002h 0004h bmtimel equ bmtimel equ 0004h afptime equ 0006h ; ポビュレーション変更用AFP bmcoolt equ 000ah ; ピーム クーリング タイム rftimel equ 000ch rftime2 equ 000eh rfkillt equ 0010h ; RFエフェクト キル

cttime1 equ cttime2 equ

cttime3 equ

cttime4 equ cttime5 equ

cttime6 equ

キルタイム

0012h 0014h

0016h

0018h 001ah 001ch  RFの点数の番地
 RFデータの先頭番地
 計測データU1の先頭番地 D1 計測データU2の先頭番地 D2 SEMデータの先頭番地 待時間データの先頭番地 ループ数の先頭番地 データアドレスの退避番地

パラメータの数\*2

1/0#-1

シンセサイザー用

1/0#-1

\*2-2 ; dummy time ; ビームonタイム ; ビームonタイム微調整

; RF onタイム ; RF onタイム微調整 カウント タイム(中) カウント タイム微調整 カウント タイム(前) カウント タイム(前) カウント タイム(後) カウント タイム微調整

```
RFデータ オフセット
bitdtl equ Oh
bitdth equ 1h
trdt equ 10h; Bit data for WAVETEK
                   ルーブ数
   lpwait equ 063Ch
63Ch or 383h 長周期WAITループ用
lpulse equ 02h
; コントロールバルス用
                     コントロール信号
     bmstart equ
bmstop equ 00010000b
screset equ 0000001b
clockl equ 0000010b
ctgate equ 00000100b
clock2 equ 0000100b
ctgrst equ 0000100b
ctgcl1 equ 0000110b
ctgcl2 equ 0000110b
workend equ 0000010b
workst equ 0100000b
rfstart equ
rfstop equ
rfon equ
afpbit equ
off equ
off
                    カウンターコントロールビット
   holdall equ
openall equ
open1 equ
open2 equ
0111111b
0111111b
                       インプットピット
 stopbit equ
beamon equ
beamoff equ
fton equ
ftoff equ
ftoff equ
ftoff equ
0100000b
ftoff equ
0100000b
ftoff equ
0100000b
ftoff equ
0100000b
                       シンセサイザーコントロールストロポ
remoton equ 10111111b
remoff equ 1111111b
stroff equ 1000000b
str01 equ 10000001b
str10 equ 10000010b
str1k equ 10000100b
str100k equ 1001000b
strDB equ 10110000b
     ______
  code segment
assume cs:code,ds:code
                             マクロ部インクルード
                             include lib"iocntr.asm
                          プログラムスタート
    begin:
                          レジスタの退避
                              push ds
push es
push ax
push bx
push cx
push di
push di
push si
push bp
                              割り込みのマスク
                           mov dx,02h
mov al,7fh
out dx,al
mov dx,0ah
mov al,0efh
out dx,al
mov dx,1fh
mov dx,1fh
mov dx,al
                             引数の受け渡し
                              mov bp,bx
mov di,adnlp
mov cx,nparal
    loop0
                              mov
                                                                bx,ds:[bp]
                              mov ds:[di],bx
add di,0002h
add bp,0002h
loop loop0
   $
                             mov bp,adnlp
les si,ds:dword ptr [bp]
                                mov cx,es:[si]
```

	xy = y = v) th MIL
count	er hold ·
ctrese	t
1 224	セサイザー・remote
	-l
mov d out d	lx,synthe x,al
gloop	
9.00p	push cx
	mov bp,adwork mov di,adnrf
11	mov cx,npara2
toop1	mov bx,ds:[bp]
	mov ds:[di],bx
	add di,0002h
	loop loop1
;	mov bp,adnrf
	les si,ds:dword ptr [bp]
	mov cx,es:[si]
	%out 3
	メインルーチン
;	
LA	B2CNTR.ASM
; 1995	.10.12 modified WAVETEK co
;	終了処理部
;	DOD CX
	dec cx
	jcxz retn
	jmp gloop
	エラー、ストップ時のフラグセット
; (ercl	heck マクロ内より)
erretn	
	les si,ds:[bp]
	mov es:[si],cx
	PASICO DAL
2	15 /1 5 1 1 / 5 / / 19 26
	BASIC CONTRACT
retn:	DASICOVIZM
retn:	bitcntr bmport,off
retn:	bitentr bmport,off セサイザー remote
retn:	bitcntr bmport,off セサイザー remote al.remoff
retn:	bitcntr bmport,off セサイザー remote al,remoff IX,synthe
mov mov di	bitcntr bmport,off セサイザー remote al,remoff ix,synthe x,al
mov mov dout d:	bitcntr bmport,off セサイザー remote al,remoff x,synthe x,al 割り込みマスクの解除
mov mov cout d:	bitcntr bmport,off セサイザー remote al,remoff x,synthe x,al 割り込みマスクの解除 mov. dx 02b
retn:	bitcntr bmport,off セサイザー remote al,remoff ix,synthe x,al 割り込みマスクの解除 mov dx,02h mov dx,02h
mov mov mov di	bitcntr bmport,off とサイザー remote al,remoff ix,synthe x,al 割り込みマスクの解除 mov dx,02h mov dx,0ah
mov mov dout di	bitcntr bmport,off とサイザー remote al,remoff x,synthe x,al 割り込みマスクの解除 mov dx,02h mov dx,02h mov dx,0ah mov dx,0ah mov dx,0ah
mov mov cout di	bitcntr bmport,off とサイザー remote al,remoff kx,synthe x,al 割り込みマスクの解除 mov dx,02h mov dx,02h mov dx,0ah mov dx,0ah mov dx,0ah mov dx,0ah mov dx,0ah mov dx,16h
mov mov cout d:	bitcntr bmport,off とサイザー remote al,remoff kx,synthe x,al 割り込みマスクの解除 mov dx,02h mov dx,02h mo
i i i i i i i i i i i i i i i i i i i	bitcntr bmport,off とサイザー remote al,remoff kx,synthe x,al 割り込みマスクの解除 mov dx,02h mov dx,02h mo
i setn: i setn: i setn: i mov mov out d: i	bitcntr bmport,off eサイザー remote al,remoff ix,synthe x,al 割り込みマスクの解除 mov dx,02h mov dx,04h mov dx,04h mo
i i i i i i i i i i i i i i i i i i i	bitcntr bmport,off とサイザー remote al,remoff ix,synthe x,al 割り込みマスクの解除 mov dx,02h mov dx,04 mov dx,04 mo
i i i i i i i i i i i i i i i i i i i	bitcntr bmport,off とサイザー remote al,remoff ix,synthe x,al 割り込みマスクの解除 mov dx,02h mov dx,02h mov dx,0ah mov dx,0ah mov dx,1fh mov dx,al mov dx,al 通道レジスタの復帰 pop bp pop si pop bp pop di
i i i i i i i i i i i i i i i i i i i	bitcntr bmport,off とサイザー remote al,remoff ix,synthe x,al 割り込みマスクの解除 mov dx,02h mov dx,02h mov dx,0ah mov dx,0ah mov dx,1fh mov dx,1fh mov dx,1fh mov dx,1fh mov dx,1fh mov dx,1gh mov dx,1gh pop bp pop si pop di pop dx
i i i i i i i i i i i i i i i i i i i	bitcntr bmport,off とサイザー remote al,remoff kx,synthe x,al 割り込みマスクの解除 mov dx,02h mov dx,02h mov dx,0ah mov dx,al Bab Saturbar
i jezz- i jezz- jez - jez- jez	bitcntr bmport,off とサイザー remote al,remoff kx,synthe x,al 割り込みマスクの解除 mov dx,02h mov dx,02h mov dx,0ah mov dx,0ah mo
i syr	bitcntr bmport,off とサイザー remote al,remoff ix,synthe x,al 割り込みマスクの解除 mov dx,02h mov dx,02h mov dx,0ah mov dx,al pop bp pop dx pop dx pop es pop ds pop ds
i i i i i i i i i i i i i i i i i i i	bitcntr bmport,off とサイザー remote al,remoff x,synthe x,al 割り込みマスクの解除 mov dx,02h mov dx,02h mov dx,01h out dx,al mov dx,0ah mov al,00rh out dx,al mov dx,0ah mov al,00rh out dx,al mov dx,0ah mov dx,0ah s,000 dx pop bp pop dx pop dx pop ds s proc far
i j yyy. mov cout di i j ; ; ; ; ;	bitcntr bmport,off とサイザー remote al,remoff kx,synthe x,al 割り込みマスクの解除 mov dx,02h mov al,01h out dx,al mov dx,0ah mov al,0erh out dx,al mov dx,0ah mov al,0erh out dx,al mov dx,0ah mov al,0erh out dx,al mov dx,0ah mov al,0erh out dx,al mov dx,0ah mov dx,0ah s,0erh out dx,al s, sproc far iret s endp
i yyy. mov cout di	bitcntr bmport,off とサイザー remote al,remoff kx,synthe x,al 割り込みマスクの解除 mov dx,02h mov al,01h out dx,al mov dx,0ah mov al,0e7h out dx,al mov dx,0ah mov al,0e7h out dx,al 通道レジスタの復帰 pop bp pop si pop di pop bx pop cx pop es pop es pop ds s proc far iret s endp ande
i syr mov out di i i retba retba	bitcntr bmport,off セサイザー remote al,remoff kx,synthe x,al 割り込みマスクの解除 mov dx,02h mov dx,00h out dx,al pop bp pop bi pop bx pop bx pop bx pop bx s proc far iret s endp ends
i syy- mov cout di i si retba code if2	bitcntr bmport,off とサイザー remote al,remoff ix,synthe x,al 割り込みマスクの解除 mov dx,02h mov dx,0ah mov dx,0ah mov dx,0ah mov dx,1fh mov dx,al 迎直レジスタの復帰 pop bp pop si pop bp pop cx pop bs pop cx pop bs pop cx pop bs pop cx pop cx pop bs pop cx pop cx

### IOCNTR.ASM マクロルーチンライブラリ for LABCNTR SYSTEM by A. Kitagawa 1991/01/25 modified by T. Miyake to use New Synthesizer 1994/1/25 1994/11/18 CAMAC MI %out IOCNTR v.11.00 l.01 %out BEAM\*2 mode %out 1 LBL & VdG System -----ビットコントロール:1/0ポートにビットをたてる port :ボートアドレス data :8ピットのデータ bitcntr macro port,data push dx mov dx,port mov al,data out dx,al pop dx endm 制御バルス:1/0ポートよりパルスを送出する adrs :ポートアドレス before :送出時のビット after :送出後のビット length :パルス長 (定周期ループの回数) bpcntr macro adrs, before, after, length r mario adisoe even mov dx,adrs mov dl,before out dx,al wtloopc length mov al,after out dx,al pop dx endm ビームウェイト:設定したビットが入力されるまで待機 xx :設定ビット (0:マスク、1:設定) inport :インブットボート wait macro xx local wait even push mov dx dx,inport wait in al.dx and al.xx mov ah.00h cmp ah.al jz wait pop dx endm エラーチェック:エラーフラグメモリを調べ、条件分岐 adrs :エラーフラグの格納番地 erretn :エラー時の飛び先 ercheck macro adrs local cont mov bp,adrs les si,ds:[bp] mov ax,0000 cmp ax,es:[si] jz cont jmp erretn cont; cont: endm エラーストップ検出:入力信号を指定フラグに積算する port :エラーの入力ポート frg :エラーフラグのマスク (0:マスク) adrs :エラーフラグの格納番地 ah :入力信号以外のエラー errin macro port,adrs,frg mov dx,port in al,dx and ax,frg mov bp,adrs les si,ds:[bp]

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```
or es:[si],ax
endm -
                            .
            定周期ループ:指定回数、空ループする
              wtime :ループ回数
    wtloopc macro wtime
local loop3
even
push cx
mov cx,wtime
   loop3
            loop loop3
pop cx
endm
            短周期ループ:指定したアドレス内の回数、空ループする
              adwtlp :ループ回数格納番地の先頭
wtime :オフセット
  wtloop macro wtime
local loop3
even
nop
push es
push si
push bp
mov bp,adwtlp
les si,ds:[bp]
add si,wtime
mov cry.ses[si]
                    n cx
n es
n si
bp,adwtlp
si,ds:[bp]
si,wtime
             mov
                       cx,es:[si]
   loop3
            loop loop3
pop bp
pop si
pop es
pop cx
endm
            長周期ループ:二重ループ
             adwtlp :ルーブ回数格納番地の先頭
wtime1 :オフセット (大ループ)
wtime2 :オフセット (小ループ)
              lpwait :空ループの回数 (大ループ)
     vtloopl macro wtime1,wtime2
local loop3
local loop4
local loope
            push cx
push cs
push si
push bp
mov bp,adwtlp
les si,ds:[bp]
add si,wtime1
add
mov
jcxz
loop3:
                       cx,es:[si]
loope
             push
mov
                       cx
cx,lpwait
   loop4
                       loop4
cx
loop3
            loop
pop
loop
            pop bp
pop si
pop es
pop cx
wtloop wtime2
endm
    データ取り込み: CAMACよりデータを取り込む.
    xx:データ格納アドレス
           yy:チャンネル番号
  in'data macro xx,yy
local exit
local exit2
local carry
push dx
push si
push si
push es
push es
push bx
   push bx
  ii
cmcset yy,SCALLER1
cmcread rddt
mov bh,00h
shl bx,1h
mov bp,xx
          les si,ds:dword ptr [bp]
add ax,es:[si]
jc carry
```

jns exit inc bx sub ax,8000h jmp exit2 carry: inc bx bx exit: nop nop exit2: mov es:[si],ax add bx,es:[si+2] add bx,es:[si+2] mov es:[si+2],bx pop bx pop es pop ds pop si pop bp pop dx endm RFデータ転送、RF出力 (I/O controll sub routine): 指定番地の内容を出力 ad :ボートアドレス n :出力データのオフセット si reg :RF data address dtout macro ad,n push di mov di,si add di,n mov al,es.[di] mov dx,al pop di endm (Bit Out mode): r f ポートにデータを出力 bitout macro dtout rfbitpl,bitdtl bitcntr rfbitpl,00h endm WAVETEK 5135A mode:シンセサイザーコントロール dtsend macro adr mov al,es:[si] mov a mov dx,adr out dx,al inc si inc si endm strsend macro stdt local wait mov dx.syntstr mov al.stdt out dx.al mov cx.02h wait: loop wait mov al.stroff out dx.al endm trdtout macro adrs push cx mov bp,adrs les si,ds:dword ptr [bp] add si,trdt disend syntlook strsend strlook disend syntlk strsend syntlk disend syntlo strsend strlo disend syntlon strsend strOl disend syntlom strsend strDB ii エラーストップ検出 errin inport,aderror,errfrg pop cx endm (main routine) rfdata :r í データの先頭番地 aderror :エラーフラグの格納番地

errfrg :エラーフラグ rfdtout macro rfdata even push push push push dx bp si ds es trdtout rfdata エラーストップ検出 errin inport,aderror,errfrg pop pop pop pop endm es ds si bp dx カウンターオープン,ホールドセレクト hldsel :セレクトフラグ open:全chオーブン その他 :全chオールド counter macro hldsel counter macro hidse local openall local other mov al.hidsel cmp al.open jz openall seti jmp other openall: clri other: endm カウンターリセット ctreset macro execc endm r f 制御セクション rfcntr macro before,after,t1,t2 even bpcntr rfport,rfstart,rfoff,lpulse bitcntr rfport,before in data adctu1,ctch1 in data adctu2,ctch3 in data adctd2,ctch3 et treset wtloopl t1,t2 bitcntr rfport,after bpcntr rfport,rfstop,after,lpulse endm アドレスインクリメント n :インクリメント量 adrsinc macro adress,n push bp push si push ds mov bp,adress mov si,ds:[bp] add si,n mov [bp],si pop ds pop si pop bp endm mov pop pop endm アドレスデクリメント n :デクリメント量 adrsdec macro adress,n push bp push si push ds mov bp,adress mov si,ds:[bp] mov sub mov pop pop pop endm si,ds:[b si,n [bp],si ds si bp

.

カウントセクション (sub routine) (main routine) section :出力されるセクションナンパー n :not use ni :データアドレスのインクリメント量 t1 :時間パラメータのオフセット t2 : unt macro section,n,ni,t1,t2 even bitcntr secport, section bitcntr secport,sec counter open bitcntr ctport,ctgate adrsinc adctul,ni adrsinc adctul,ni adrsinc adctul,ni wiloopi t1,t2 bitcntr ctport,off counter hold bitcntr secport off bitcntr secport,off endm ビームクーリングセクション ool macro even wtloop bmcoolt endm rfキルセクション rfkill macro even wtloop rfkillt endm rfデータアドレスのインクリメント rfadinc macro even adrsinc adrfdt,0020h endm r fデータアドレスのインクリメント2 rfadinc2 macro even adrsinc adrfdt,0040h endm r 「データアドレスのインクリメント3 rfadinc3 macro even adrsinc adrfdt,0060h endm r f データアドレスのインクリメント 4 rfadinc4 macro even adrsinc adrfdt,0080h endm rfデータアドレスのデクリメント rfaddec macro even adrsdec adrfdt,0020h endm r fデータアドレスのデクリメント 2 rfaddec2 macro even adrsdec adrfdt,0040h endm r fデータアドレスのデクリメント 3 rfaddec3 macro even adrsdec adrfdt,0060h endm

r f データアドレスのデクリメント4 rfaddec4 macroeven adrsdec adrfdt,0080h endm データアドレスのインクリメント ctadinc macro n even adrsinc adctul,n adrsinc adctd1,n adrsinc adctu2,n adrsinc adctd2,n endm カウントデータの読み込み ountin macro even in data adctu1,ctch1 in data adctd1,ctch2 in data adctu2,ctch3 in data adctd2,ctch4 ctreset SEM取り込み:SEMパルスの積算 xx :SEMの格納アドレス yy :SEM読み込みのチャンネル番号 ; st`sem macro ctreset counter open endm in'sem macro xx,yy local exit local exit local carry even push dx push bp push si push ds push es push es push bx ii mov bp,xx les si,ds:dword ptr [bp] ii counter hold cmcset yy,SCALLER2 cmcread rddt mov bh,00h shl bx,1h add ax.es:[si] add ax,es:[si] jc carry jns exit inc bx sub ax,8000h jmp exit2 carry bx bx inc exit: nop nop exit2: mov es:[si],ax add bx,es:[si+2] mov es:[si+2],bx ctreset pop bx pop bs pop bp pop dx endm i exit2: st'beam macro ctreset counter open endm in beam macro xx,yy1,yy2

push dx push bp push si push ds push es push bx counter hold in beam2 xx,yy1,00h in beam2 xx,yy2,04h ctreset pop bx pop es pop ds pop si pop bp pop dx endm in beam2 macro xx,yy,zz local exit local exit2 local carry mov bp,xx les add si,zz si,ds:dword ptr [bp] cmcset yy,SCALLER2 cmcread rddt mov bh,00h shl bx,1h add ax,es:[si] jc carry jns exit inc bx sub ax,8000h jmp exit2 carry: inc bx bx exit: nop nop exit2 mov es:[si],ax add bx,es:[si+2] mov es:[si+2],bx endm ; camac macro routines A Command set (break ax) : cmcset macro a,N mov al,N ;set station number N mov ah,a ;set sub address A out nacmnd,ax ;write N,A to Command endm Data Read (blj-data high 8bit,axj-data low 16bit) cmcread macro f local ckdone in ax,status ;read Status and ah,lint ei'i ;clear noX,noQ mov al,f ;set F (Read LAM reg-mask n) out contrl,ax ;write F to Command out camacgo,al ;Camac Go Command ckdone: in ax,status ;read Status test ah,done ;check Done jz ckdone ;if not done then wait in ax,datahi ;read Data high mov bx,ax mov bx,ax in ax,datalow ;read Data low endm ; set I (inhibit line) cycle seti macro in ax,status and ah,lint ei'i ;hold LINT,EI,I or ah,l'line ;set I out contrl,ax endm ; clear I (inhibit line) cycle ; clri macro in ax,status and ah,lint'ei ;hold LINT,EI out contrl,ax endm ; execute C (clear) cycle execc macro

in ax,status and ah,lint'ei'i ;hold LINT,EI,I or ah,c'line ;set C out contrl,ax endm -----%out 2

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