

^{13}C NMR Investigations of Spin–Lattice Relaxation in 99% ^{13}C -Enriched Diamonds

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The paper is devoted to investigations of spin–lattice relaxation processes in 99% ^{13}C -enriched diamonds. Relaxation time measurements were performed as a function of orientation, magnetic field, and temperature. Both experimental results and theoretical discussion are presented. Multiexponential behavior of nuclear magnetization recovery was observed. There was found no significant influence of the diamond orientation on the nuclear spin–lattice relaxation. The field dependence of the spin–lattice relaxation time was found to be proportional to the second power of the magnetic field. The temperature measurements showed a weak increase of the spin–lattice relaxation time with decreasing temperature. Possible mechanisms of impurity relaxation are considered and compared with the experimental data. © 1998 Academic Press

INTRODUCTION

Diamonds exhibit a wide range of spin–lattice relaxation times (Table 1). The spin–lattice relaxation takes place due to the process where lattice vibrations induce transitions in the ^{13}C nuclear system via nuclear interactions with another ^{13}C nucleus or a trapped paramagnetic atom. Consequently, in a gem diamond the spin–lattice relaxation time is very long since interactions between the naturally abundant ^{13}C nuclei are very weak and the concentration of impurities is low. In synthetic diamonds the impurity concentration can be much higher than it is in gem diamonds. This leads to faster relaxation. In ^{13}C -enriched diamonds with low impurity concentration the dipole–dipole interactions between neighboring ^{13}C nuclei will accelerate relaxation in comparison to natural ^{13}C abundance diamonds with low impurity concentration.

Thus, the nuclear spin–lattice relaxation time T_1 in diamonds is determined by two contributions (10)

$$\frac{1}{T_1} = \frac{1}{T_1^{\text{lat}}} + \frac{1}{T_1^{\text{imp}}}, \quad [1]$$

where T_1^{lat} is the lattice component of the spin–lattice relax-

ation determined by nuclear dipole–dipole interactions for spin- $\frac{1}{2}$ nuclei and T_1^{imp} is the impurity component of the spin–lattice relaxation time determined by ^{13}C nuclear interactions with paramagnetic centers. The first term in Eq. [1] usually can be considered negligibly small—according to the theory of Waller (11). For a material with 100% ^{13}C enrichment the thermally induced lattice vibrations only modulate the nuclear dipole–dipole interactions marginally, leading to relaxation times T_1^{lat} much longer than the impurity contribution. Therefore, relaxation time in diamonds is mostly determined by the trapped paramagnetic impurities. The model for impurity relaxation is the following: (i) the relaxed electrons of a paramagnetic impurity relax very effectively nearby ^{13}C spins; (ii) these ^{13}C spins in turn relax their ^{13}C neighbors further away from the impurity via energy-conserving ^{13}C – ^{13}C spin–spin flip-flops. This is referred to as the mechanism of nuclear impurity relaxation accompanied by spin diffusion (10, 12, 13).

Experimentally, the spin–lattice relaxation time T_1^{imp} describes the exponential buildup of ^{13}C magnetization along the external magnetic field to its equilibrium value. Nevertheless, for samples with natural or low abundance of ^{13}C the spin diffusion between the nuclei is negligibly small, so that the relaxation rate of individual ^{13}C spins is determined by the distance between the ^{13}C spin and the nearest paramagnetic impurity. The ^{13}C spins close to the impurity have short relaxation times and those further away have much longer relaxation times. This leads to a distribution of relaxation rates over the sample resulting in a nonexponential spin–lattice relaxation, which can be fitted to a stretched exponent (7, 14, 15). A distribution of relaxation rates over the sample gives rise to the t^X behavior of magnetization recovery

$$M(t) = M_0(1 - e^{-(t/T_1^{\text{imp}})^X}) \quad [2]$$

where X is a factor between 0.5 (the vanishing spin diffusion limit) and 1 (the complete spin diffusion limit).

TABLE 1
Spin-Lattice Relaxation Times in Diamonds

Sample	^{13}C abundance	T_1	Ref.
Pure synthetic diamond	99%	5 hours	(1)
Gem diamond	Natural	3.5 days	(2)
Natural diamond	Natural	300 s	(3)
Natural diamond	Natural	2 hours	(4)
Synthetic diamond	Natural	220 s	(4)
Synthetic diamond	Natural	1 s	(2)
Semiconducting diamond	Natural	4 hours	(5)
Diamond film	Natural	70 s	(6)
Diamond film	50%	17 s	(6)
Diamond film	100%	8 s	(6)
CVD diamond film	Natural	55 s	(7)
CVD diamond film	Natural	1000 s	(8)
CVD diamond film	14%	22 s	(8)
Different CVD diamond films	22%	1–20 s	(9)

A number of experimental studies devoted to the spin-lattice relaxation in diamond-like carbons show correlation with Eq. [2]. For example, in order to check the vanishing spin diffusion limit the magnetization recovery behavior has been studied in an industrial diamond under MAS conditions in order to suppress the small dipolar interactions, which can cause spin diffusion (2). Over the short time period observed, the magnetization indeed changes proportional to $t^{1/2}$, as follows readily from Eq. [2] for $X = 0.5$, when the exponent is expanded as an infinite series and only the first two terms are retained. By using the DNP (dynamic nuclear polarization) NMR experiment the same $t^{1/2}$ magnetization recovery behavior has been found in natural and synthetic diamonds, as well as in ^{13}C natural abundant and 14% ^{13}C -enriched diamond films (3, 4, 7, 8).

Contrary to the theory described above there are some experimental results which cannot be explained. For example, the t^1 magnetization recovery behavior has been found in a pure ^{13}C natural abundant diamond with about 10^{16} cm^{-3} concentration of paramagnetic impurities (5): (i) on the one hand, the magnetization recovery shows that spin diffusion plays a vital role in transferring magnetization within the spin system; (ii) on the other hand, it is hard to believe in effective spin diffusion for ^{13}C naturally abundant diamonds. The same single exponential behavior of magnetization recovery was also found for three diamond films with different ^{13}C concentrations (1.1, 50, and 100%) (6), reflecting that the spin diffusion mechanism still plays a role for the ^{13}C natural abundance sample, and the different diffusion rates for the different abundances were reflected in different relaxation times (see Table 1). Disagreement between the experimental results and the theory has prompted additional studies to be carried out.

For more detailed experimental investigation of the spin-

lattice relaxation mechanisms a 99% ^{13}C -enriched diamond has been chosen. The 99% ^{13}C -enriched diamond is a relatively new material. Single crystals of diamonds of any desired ^{13}C - ^{12}C ratio can now be grown as a result of recent developments in diamond synthesis (16, 17). Several fundamental studies have addressed the consequences of the isotopic composition of diamonds, e.g., thermal conductivity (18), Raman spectrum (19, 20), lattice parameter (21), vibrational and defect-associated local modes (22), indirect electron band gap (23), and elastic constants (24). One of the most interesting features in the 99% ^{13}C -enriched diamond is that the enhanced atomic mass means a reduced lattice parameter (21), which leads to slightly enhanced elastic constants (24) (elastic moduli deduced from the Brillouin shifts experienced by inelastically scattered monochromatic radiation are approximately 0.5% higher than the corresponding values for a natural diamond). The conclusion from this result is that such a diamond is the hardest material known.

The first NMR data on the 99% ^{13}C -enriched diamond were reported by Lefmann *et al.* (25). A more detailed study of ^{13}C orientation-dependent NMR lineshapes and spin-spin relaxation times in these diamonds can be found in (26). Preliminary investigations of spin-lattice relaxation time as a function of orientation showed a weak influence of the crystal orientation on the spin-lattice relaxation time (1). Comparison between spin-lattice relaxation times for colorless and greenish 99% ^{13}C -enriched diamonds lead to the conclusion that the major relaxation mechanism in greenish diamonds is via paramagnetic impurities.

This paper represents a full investigation of the ^{13}C spin-lattice relaxation mechanism in single crystal 99% ^{13}C -enriched diamonds. The experimental behavior of ^{13}C spin-lattice relaxation times as a function of crystal orientation, static magnetic field, and temperature is reported. The data are discussed based on a theory adapted for the studied diamond.

EXPERIMENTAL

A greenish 99% ^{13}C -enriched diamond was investigated (synthesized by H. Kanda, National Research in Inorganic Materials, Japan). The sample was synthesized at high pressure and high temperature using a Ni catalyst containing a few percent Ti. The resulting diamond of 30 mg had a pyramidal shape, with four [111] faces and a [001] base. The ESR spectrum of the diamond reflected the presence of a large variety of paramagnetic atoms.

Investigations of orientation- and temperature-dependent relaxation were carried out in a Bruker MSL300 spectrometer in a constant magnetic field of $B_0 = 7 \text{ T}$, which corresponds to a ^{13}C nuclear Larmor frequency $\nu_0 = 75.468 \text{ MHz}$. Ninety degree pulses were adjusted to $5.5 \mu\text{s}$. Spectral width

was 10^5 Hz. Dead time delay equal to $2 \mu\text{s}$ and recycle delay equal to 30 s are used. Spectra were sampled in 512 W or 2K data points. A Doty goniometer probehead DSI418 was used for the investigations. Diamond samples were mounted by Apiezon T grease in Al_2O_3 semicubes. The rotation of the crystal was around the axis perpendicular to the [110] diamond structure plane. The initial crystal orientation was determined by optical goniometry.

The experiments for different magnetic fields were performed in Bruker 200-, 250-, 300-, and 500-MHz and Varian 400-MHz spectrometers. Each spectrum was acquired by accumulating 80 scans at low magnetic fields. At higher magnetic fields (on 400 and 500-MHz spectrometers) 4 scans were enough for good signal/noise ratio.

Measurements of spin–lattice relaxation times were performed using the magnetic saturation recovery method. It was found that the experimental saturation recovery curve cannot be approximated for neither a single exponent nor a stretched exponent. The experimental points were found to fit to at least three different exponential contributions. These contributions will be referred to as “fast,” “medium,” and “slow” in the following discussion.

GENERAL THEORETICAL CONSIDERATION OF SPIN-LATTICE RELAXATION IN ^{13}C DIAMONDS

Since the ^{13}C spin–relaxation times in the greenish ^{13}C diamonds were found to proceed much more rapidly than in the colorless diamond (I) the model of nuclear relaxation via paramagnetic impurities will be considered for the diamond under study. Taking into account Eq. [1] it follows that the lattice contribution to the relaxation is negligible in comparison with the impurity term, and the value obtained for the greenish samples may be taken as $T_1 = T_1^{\text{imp}}$. It should be noted that the term “paramagnetic impurities” cover all possible kinds of paramagnetic defects with nonzero magnetic moment. The relaxation via paramagnetic impurities will be further referred as “impurity relaxation.” This relaxation is obviously dependent on impurity concentration in the sample, and therefore two possible situations can be distinguished: (i) the concentration of impurities is high enough that interactions between impurities should be considered and every nucleus should “feel” more than one impurity; (ii) the concentration of impurities is small enough that interactions between each impurity and surrounding atoms dominate over the impurity–impurity interactions, which can be neglected in that case. The first possibility is usually valid for samples purposely made to have high impurity concentrations (12, 13, 27). The industrial production results in concentration of unwanted impurities not more than 10^{18} cm^{-3} . Here interactions between impurities can be neglected. Therefore, for the diamonds under study the case of noninteracting impurities will be considered.

For the case of noninteracting paramagnetic impurities the spin–lattice relaxation process should be considered based on a model consisting of one paramagnetic center interacting with surrounding ^{13}C nuclei. The nuclear impurity relaxation takes place via two processes: (1) nuclear relaxation with the time $T_1^i(r)$ due to direct interaction with the paramagnetic impurity (which is dependent on distance between nuclei and impurity as r^{-6}), and (2) nuclear spin diffusion with the diffusion tensor D . Assuming isotropic diffusion for one paramagnetic center the relaxation of nuclear magnetization M to its equilibrium value M_0 should be described by a combination of equations for these two processes (12, 13):

$$\frac{\partial M}{\partial t} = D\Delta M - \frac{M - M_0}{T_1^i(r)}. \quad [3]$$

Description of the relaxation process of the entire sample requires magnetization averaging over the sample volume. As can be shown from a detailed mathematical analysis (12, 13) Eq. [3] leads to the exponential relaxation of the average over the volume magnetization $\langle M \rangle$ with the relaxation time T_1^i :

$$\frac{\partial \langle M \rangle}{\partial t} = -\frac{\langle M \rangle - M_0}{T_1^i}. \quad [4]$$

The relaxation time T_1^i is a function of paramagnetic impurity concentration N , of the nuclear relaxation time at the unit distance from the impurity $T_1^i(r = 1) = C^{-1}$, and of the spin diffusion coefficient D .

The relaxation time T_1^i is significantly influenced by the diffusion barrier with radius d , which can be described by the step function: $D(r \geq d) = D$ and $D(r < d) = 0$. This is due to a large shift of the ^{13}C nuclear resonance line in the vicinity of paramagnetic centers. In the vicinity of the center the flip-flop transitions are not possible, and the spin diffusion process decreases significantly. The magnetic field created by a paramagnetic center is on the order of $\hbar\gamma_s/r^3$. The NMR linewidth is on the order of $\hbar\gamma/a^3$ —the magnetic field caused by a neighboring nucleus situated at a distance a . The radius d can be defined as the distance from the paramagnetic center, where the magnetic field due to the center is equal to the NMR linewidth. Therefore, $d \approx (\gamma_s/\gamma)^{1/3}a$. Nuclei within the radius d will be referred to as “diffusion unobservable nuclei” since due to their frequency shift they will not contribute to the NMR line averaged over the volume.

Also since impurity concentration is small the main contribution to the NMR signal should be mostly from nuclei, which are situated far from the impurity, namely the nuclei, which relax only due to spin diffusion. The next important parameter determining T_1^i is the distance $b = 0.68(C/D)^{1/4}$ (12). b is

the distance from the impurity, where probability of nuclear transitions due to interaction with an impurity is equal to probability of nuclear flip-flop transitions. In other words, at $r \geq b$ the spin diffusion is dominating over the nuclear relaxation, while at $r < b$ the nuclear relaxation is predominant via direct nuclear interaction with the paramagnetic center. If $d \ll b$ the diffusion barrier should not influence the spin diffusion outside d , but if $b < d$ the diffusion barrier will lead to decrease of relaxation. For $d \ll b$ the relaxation is named ‘‘diffusion limited’’ relaxation, while for $b < d$ it is called ‘‘rapid diffusion’’ relaxation. The latter reflects that the spin diffusion in the area $r > d$ is much faster than the direct relaxation due to the paramagnetic center. Indeed, within the region $b < r < d$ the spin diffusion cannot take place inside the diffusion barrier, and the direct nuclear relaxation is very inefficient because of the large distance between the center and the nuclei. In this case the nuclear system should first achieve the common magnetization due to rapid spin diffusion, and afterwards slowly achieve the equilibrium magnetization due to the weak nuclear interaction with the center. Therefore the spin-lattice relaxation time should not be influenced by the diffusion coefficient D .

The expressions for the relaxation time T_1^i for (a) diffusion limited relaxation and (b) rapid diffusion relaxation (12) can be written as

$$\frac{1}{T_1^i} = 8.5 NC^{1/4} D^{3/4} \quad [5a]$$

$$\frac{1}{T_1^i} = \frac{8.5 NC}{d^3}. \quad [5b]$$

At a given magnetic field and temperature the choice between the two situations is fully dependent on the nature of paramagnetic impurities and positioning of the observed nuclear isotopes in the sample. Since the variety of impurities in the studied diamond is very large, it will be necessary to analyze the experimental results first and to select the appropriate mechanism of the two in Eqs. [5] based on comparison with the experimental data.

THEORETICAL PREDICTIONS OF ORIENTATION-DEPENDENT T_1

Since dipole interactions nuclei-nuclei and nuclei-paramagnetic center are strongly dependent on the angle between the direction of the interaction and the constant magnetic field there are three values that can depend on crystal orientation in Eqs. [5]: C , d , D .

If the diffusion-limited relaxation is relevant it will be useful to discuss the spin diffusion coefficient D . In general, the spin diffusion coefficient is a symmetrical second-rank tensor. We shall start from an example of equivalent nuclei,

which can be used for cubic lattice or powder samples when D becomes a scalar. In that case, taking into account the flip-flop transitions of the nuclear nearest neighbors, D can be estimated as (13)

$$D \approx Wa^2 \approx \frac{a^2}{30 T_2}, \quad [6]$$

where W is the flip-flop transition probability of the nuclei, a is the distance between the nuclei, and T_2 is the nuclear spin-spin relaxation time. Usually for solid state $T_2 \approx 10^{-5}$ s and $a = (2-3) \times 10^{-8}$ cm. That will give a spin diffusion coefficient $D \approx (1-3) \times 10^{-12}$ cm 2 s $^{-1}$.

Equation [6] can be useful for estimates of the diffusion coefficient along some of the crystal axes in the diamond. These estimates should give an idea about how big the difference in the spin diffusion coefficient for the ^{13}C diamond at different crystal orientations can be, i.e., how should the spin-lattice relaxation time be influenced by the crystal orientation. To answer this question three characteristic orientations for the greenish diamond (25, 26) will be considered: magic angle orientation $B_{0\parallel}[100]$, and $B_{0\parallel}[111]$ and $B_{0\parallel}[110]$. For the magic angle orientation the dipole-dipole interactions between the nearest neighbors are zero; therefore, for estimation of D the distance a in Eq. [6] should be taken as the distance between the next nearest neighbors. For the diamond structure this distance is equal to 2.51 Å. Taking into account that the T_2 for magic angle orientation equals 150 μs (26), the spin diffusion coefficient for the diamond under the magic angle orientation can be estimated as $D = 0.14 \times 10^{-12}$ cm 2 s $^{-1}$.

For another orientation the diffusion will take place between the nearest neighbors, but now the situation is more complicated because the nuclei are not situated along the line parallel to B_0 , so the diffusion will also depend on the angle between B_0 and on the bonds between each of the two neighbors. In this case the diffusion of every i nucleus is due to $j = 4$ contributions of nearest neighbors, which are influenced by $(a(1 - 3 \cos^2 \Theta_{ij})/2)^2$ angle dependence:

$$D_i \approx \sum_{j=1}^4 Wa^2 \left(\frac{1 - 3 \cos^2 \Theta_{ij}}{2} \right)^2, \quad [7]$$

where $a = 1.54$ Å, the distance between the nearest neighbors in the diamond structure. Let us estimate the diffusion coefficient for the two orientations $B_{0\parallel}[111]$ and $B_{0\parallel}[110]$. For the $B_{0\parallel}[111]$ orientation $\Theta_{i1} = 0^\circ$ and $\Theta_{i2,3,4} = 109^\circ$ so that the angular term can be written as $1 + 3/4(1 - 3 \cos^2 109^\circ)^2 = 1.36$. For the $B_{0\parallel}[110]$ orientation $\Theta_{i1,2} = 90^\circ$ and $\Theta_{i3,4} = 35.5^\circ$ so that the angular term can be written as $2/4(1 - 3 \cos^2 90^\circ)^2 + 2/4(1 - 3 \cos^2 35.5^\circ)^2 = 0.98$.

TABLE 2

Parameters and Estimated Values of the Nuclear Spin Diffusion Coefficient for the Three Diamond Orientations

	Orientation		
	$B_0 \parallel [100]$	$B_0 \parallel [110]$	$B_0 \parallel [111]$
a, Å	2.51	1.54	1.54
T_2 , μs (± 5)	150	40	40
D , $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ (± 0.02)	0.14	0.19	0.25

Taking into account that the value of the spin–spin relaxation time for these orientations is on the order of $40 \mu\text{s}$ (26) the following spin diffusion coefficients can be obtained: $D(B_0 \parallel [111]) = 0.25 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ and $D(B_0 \parallel [110]) = 0.19 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$. The estimated values of the nuclear spin diffusion coefficient for the three diamond orientations are collected in Table 2.

As is expected the spin diffusion is obtained to be slower at the magic angle orientation, but on the other hand, the difference for D between the three orientations is not significant. From Eq. [5a] the spin–lattice relaxation time is proportional to $D^{-3/4}$. Therefore, the ratio between the relaxation times due to spin diffusion at different orientations should be correspondingly 1.5:1.2:1.

A similar idea can be used by estimating the coefficients C and d , where the orientation-dependent dipole interactions between a nucleus and a paramagnetic center should be considered. Although the precise types of the impurities and defects in the sample are undetermined, some general predictions can be made. First of all, ideally, the main feature should appear when these coefficients approach zero along the directions from the paramagnetic center to the nearest nuclear neighbors of the diamond lattice at the magic angle orientation, and at the same time they should have some values along other directions. On the other hand it is impossible to check how precise the diamond lattice is in the vicinity of the defects. Most likely it is not—even a paramagnetic atom of a size little different than that of the carbon atom will already bring changes in the diamond structure. That is why it is most probable that the angle-averaged paramagnetic center interactions with the surrounding nuclei, which influence C and d , should not depend on the crystal orientation.

Consequently, Eqs. [5] should be helpful in distinguishing the relaxation mechanism in the ^{13}C diamond: (i) according to the diffusion-limited relaxation mechanism, the orientation-dependent changes in the spin–lattice relaxation time should be observed due to orientation-dependent spin diffusion (Table 2); (ii) according to the rapid diffusion mechanism no dependence of the spin–lattice relaxation time on the diamond orientation should be observed.

THEORETICAL PREDICTIONS OF THE FIELD-DEPENDENT T_1

Another way to identify the relaxation mechanism (Eqs. [5]) is to investigate the dependence of the spin–lattice relaxation time on the static magnetic field H_0 . This dependence can be obtained from the coefficient C , the inverse nuclear spin–lattice relaxation time due to direct interaction with the paramagnetic center at the unit distance from it. In this case we can consider the coefficient C without taking into account the kind of impurity, since it does not influence the C dependence on the static magnetic field. The spin–lattice relaxation time $T_1(r)$ can be calculated by taking into account interaction between the nuclear spin and the spin of a paramagnetic center situated at a distance r from the nuclei (12, 13):

$$T_1(r) = \frac{r^6}{C} \quad C = \frac{2}{5} \frac{(g\beta)^2 S(S+1)}{\tau H_0^2}. \quad [8]$$

Here β is the Bohr magneton, g is the electronic g -factor of the paramagnetic impurity, S is the angular momentum quantum number of the paramagnetic impurity electrons, and τ is the paramagnetic impurity relaxation time. It should be noted that $C/2r^6$ can be understood as the probability of the relaxation reorientation of the nuclear spin situated at a distance r from the paramagnetic center. The reorientation is due to paramagnetic center relaxation and its dipole–dipole interaction.

Combining Eq. [8] and Eqs. [5] one can obtain the field dependencies of the nuclear relaxation time for two mechanisms: T_1^i (diffusion-limited relaxation) $\sim C^{-1/4} \sim H_0^{1/2}$ and T_1^i (rapid diffusion relaxation) $\sim C^{-1} \sim H_0^2$.

THEORETICAL PREDICTIONS OF THE TEMPERATURE-DEPENDENT T_1

In our model the temperature dependence of the spin–lattice relaxation time is also included in the coefficient C . The spin–lattice relaxation is based on the varying magnetic fields introduced by lattice vibrations and influenced on magnetic spins. In the beginning it is useful to consider which kinds of relaxation transitions are more probable.

According to transition probability calculations based on the perturbation theory (28) the maximum probability corresponds to the so-called direct processes of relaxation. These processes can be obtained from the first-order perturbation theory and can be described as emission or absorption of the nuclear resonance frequency lattice phonons ω_q , due to nuclear transition between the Zeeman levels ω_0 : $\omega_q \approx \omega_0$. Nevertheless, spin transitions with absorption of one and emission of the other phonon include all the excited lattice vibrations, and therefore these processes are much more ef-

fective (29). Thus, the energy conservation law can be written as $\omega_{q'} - \omega_q \approx \omega_0$. Calculating the probability for the Raman process W_R the following expression can be obtained (13)

$$W_R \sim \int_0^{\omega_D} \frac{\omega^6 e^{\hbar\omega/k_b T} d\omega}{(e^{\hbar\omega/k_b T} - 1)^2}, \quad [9]$$

where T is the temperature of the lattice and ω_D is the Debye frequency. It is possible to make some approximations of Eq. [9] for the two limiting situations depending on the Debye temperature Θ : $T \geq \Theta$ and $T \ll \Theta$. For $T \geq \Theta$ one can obtain $W_R \sim T^2$, and $W_R \sim T^7$ for $T \ll \Theta$, where $T \ll \Theta$ means that $T/\Theta \leq 0.02$.

Diamonds have the highest Debye temperature, namely $\Theta = 1200$ K. The temperatures of our measurements are within 200–400 K. Then the ratio $T/\Theta = (0.16\text{--}0.33)$, which is not smaller than 0.02. As a result of the investigated diamond the direct nuclear spin-lattice relaxation times should have a temperature dependence weaker than T^{-7} .

The spin-lattice relaxation time is proportional to the inverse transition probability (13). Taking into account the impurity relaxation mechanism reflected in Eq. [5] the value of T_1 should be proportional to the coefficient C^{-1} and the expected temperature dependencies of the nuclear spin-lattice relaxation time according to the impurity mechanism are T_1^i (diffusion-limited relaxation) $\sim C^{-1/4} \sim T^{-N}$ ($N \leq 7/4$) and T_1^i (rapid diffusion relaxation) $\sim C^{-1} \sim T^{-K}$ ($K \leq 7$). Even if the experimental conditions do not fulfill the approximation $T \ll \Theta$ exactly, the significant difference in the temperature behavior of the two mechanisms should help to choose the most appropriate mechanism from the experimental dependencies.

MULTIEXPONENTIAL BEHAVIOR OF THE NUCLEAR MAGNETIZATION RECOVERY IN THE ^{13}C DIAMOND

Experimentally it was observed that the nuclear magnetization recovery in the ^{13}C diamond cannot be approximated neither by single nor by stretched exponential dependence. In all performed experiments the experimental points can be fitted with a good approximation to three exponential contributions with almost the same exponential weight.

These three contributions to the spin-lattice relaxation time can occur as a result of different relaxation times contributed from different areas of the sample. Taking into consideration Eqs. [5] and Eq. [8] such a situation is possible if (i) there are slightly different impurity concentrations in different parts of the sample volume and if (ii) different paramagnetic impurities are present in the sample. Both items seem to be relevant for the diamonds—(i) inspection of the greenish diamond under a microscope showed that the

greenish color is not homogeneous over the sample volume, indicating variety in the impurity concentrations, and (ii) ESR measurements show presence of impurities which cover the range of different paramagnetic atoms. It seems unlikely that three regions with different impurity concentrations are existing in diamonds; therefore it is preferable to believe that there are three types of impurities dominating in the nuclear spin-lattice relaxation in the diamonds. Nevertheless, the multiexponential relaxation is only possible if these three dominating types of impurities are anisotropically distributed within the sample volume. Isotropic distribution of different impurities in the sample will lead to a single exponential relaxation—it may be faster for nuclear magnetization to diffuse some distance to the fast relaxing paramagnetic atom than to “wait” for long relaxation of the nearest paramagnetic atom. Taking into consideration a value of the spin diffusion coefficient from Table 2, it is possible to make some conclusions about anisotropy of distribution of paramagnetic atoms in the diamonds investigated. For example, the slow relaxation time component of 280 s in the sample with the spin diffusion coefficient on the order of $10^{-13} \text{ cm}^2 \text{ s}^{-1}$ requires that the nuclear magnetization diffusing through the area $2.8 \times 10^{-11} \text{ cm}^2$ (or the distance of 550 Å) should not meet any other faster relaxing paramagnetic atom. Analogously, the middle relaxation component of 47 s requires diffusion along 220 Å free from the presence of a paramagnetic atom which allows the faster nuclear relaxation. The distance of 550 Å requires existence of the areas in the diamond where concentrations of the other impurities leading to faster nuclear relaxation are less than $0.6 \times 10^{16} \text{ cm}^{-3}$. The distance of 220 Å requires existence of the areas in the diamond where concentrations of the other impurities leading to faster nuclear relaxation are less than 10^{17} cm^{-3} . The estimated values for impurity concentrations are in accordance with the model of the noninteracting impurities used for the data description.

EXPERIMENTAL STUDIES OF THE ORIENTATION-DEPENDENT T_1 AND DISCUSSION

The 300 K temperature experiments on nuclear magnetization recovery were carried out at 17 different crystal orientations obtained by crystal rotation within 180° in the [110] diamond structure plane (26). Corresponding experimental behavior of nuclear magnetization recovery at two different orientations is shown in Fig. 1. The intensities of the experimental points presented are normalized to the intensity I_0 corresponding to the equilibrium magnetization. As clearly seen in Fig. 1, the two orientations, most different by properties, exhibit the same magnetization recovery behavior within accuracy of the experiment.

The identical behaviors of magnetization recovery have been obtained for all 12 different orientations at 300 K. At

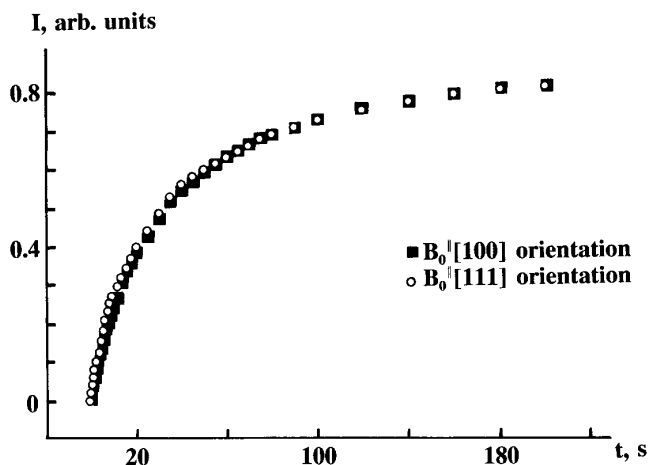


FIG. 1. Nuclear magnetization recovery curves for the two characteristic diamond orientations (■, $B_0||[100]$ orientation, and ○, $B_0||[111]$ orientation).

the other temperatures the orientation experiments have also been carried out, but only for few orientations so as to make sure that there are still no changes in magnetization behavior at different orientations at a given temperature.

The absence of T_1 orientation dependence is quite surprising—spin diffusion at magic angle orientation was expected to be slower. Nevertheless, it reflects the fact that the relaxation mechanism via the impurity is preferably due to the rapid spin diffusion mechanism. On the other hand it is possible that at the same time some of the impurities lead nuclear relaxation due to the diffusion-limited relaxation mechanism as well. For the latter relaxation mechanism the relaxation time should change in 1.5 times for the two characteristic orientations $B_0||[100]$ and $B_0||[111]$ (Table 2). In our case the nuclear magnetization recovery reflects at least three relaxation times. If a change of the relaxation times in 1.5 for all three exponential contributions is considered the difference in behaviors of magnetization recovery will be higher than the accuracy of the exponential fitting. Therefore, it would be possible to distinguish the dependence of relaxation times on orientation. If, for example, one type of impurity leads the nuclear relaxation due to diffusion-limited relaxation and the other two due to the rapid diffusion relaxation, there is a big possibility that accuracy of fitting experimental data will not be enough to feel this effect—such a change in the experimental dependence could lead to small variations of exponent weights as well as small variations of all three relaxation times within the accuracy level. If the experimental behavior in Fig. 1 is carefully inspected it can be noticed that for the smaller time periods within ~ 0 –60 s the black squares tend to be situated below white triangles, while at higher time periods they are above the triangles. Such a behavior clearly reflects some small

changes in relaxation times. Similar small features have been obtained for the other temperatures.

It can be summarized that there has been observed no significant influence of the diamond orientation on the nuclear spin–lattice relaxation processes. This means that based on the orientation data the nuclear spin–lattice relaxation is due to the rapid diffusion relaxation mechanism. It is possible that at the same time a small amount of the impurities leads nuclear relaxation due to the diffusion-limited relaxation mechanism as well.

EXPERIMENTAL STUDIES OF THE FIELD-DEPENDENT T_1 AND DISCUSSION

In order to support the mechanism of nuclear spin–lattice relaxation the influence of a constant magnetic field on the relaxation has been investigated. Since there is no influence of the crystal orientation on the spin–lattice relaxation, for simplicity of the experimental setup the data presented below were obtained at the magic angle orientation $B_0||[100]$.

Results of the experimental data of nuclear magnetization recovery for the five different spectrometers at 300 K are presented in Table 3. The values in Table 3 were obtained by computer simulation of the experimental points to three exponential contributions with their weights and relaxation times. Due to experimental and computational errors the uncertainty of 10% for the fast and medium components and the uncertainty of 20% for the slow component should be taken into account in Table 3.

One can see from Table 3 that the exponential weights vary within the accuracy of calculations, reflecting the same ratio between the exponential contributions for all magnetic fields, or in other words reflecting the same ratio between different paramagnetic impurities in the diamond in any magnetic field. This is perfectly acceptable. If the behavior of the relaxation times is followed, they are obviously increasing as the magnetic field increases. Such a behavior is in accordance with the theory of impurity relaxation (Eqs. [5] and Eq. [8]). The difference in the relaxation time behaviors for diffusion-limited relaxation and rapid diffusion relaxation is determined by the variation in rate of the relaxation time with the field. For the diffusion-limited relaxation the magnetic field should be proportional to the relaxation time in the second power, while for the rapid diffusion relaxation the magnetic field should be proportional to a square root of the relaxation time.

In Fig. 2a the obtained behavior of the fastest T_1^1 and the medium T_1^2 relaxation time components as functions of the magnetic field are presented (Table 3). The slowest component is not shown since it reflects the same type of behavior only with a bigger error. In Figs. 2b and 2c the experimental points are also shown in the scales of $(T_1^1)^2$, $(T_1^2)^2$, $(T_1^1)^{1/2}$, $(T_1^2)^{1/2}$. From the scaled data it should be seen which of the

TABLE 3
Exponential Weights and Relaxation Times Fitting to Experimental Data of Nuclear Magnetization Recovery for the Five Different Magnetic Fields

^1H frequency, MHz	Fast component		Medium component		Slow component	
	Exp. weight	T_1^1	Exp. weight	T_1^2	Exp. weight	T_1^3
200	36	4	30	16	34	110
250	33	8	40	24	27	157
300	35	9	30	47	35	280
400	39	15	32	138	29	2500
500	37	28	33	200	30	5000

two relaxation mechanisms is taking place according to the dependence of the nuclear relaxation on the magnetic field: for the diffusion-limited relaxation the $(T_1^{1,2,3})^2 \sim H_0$ proportionality should be valid, while for the rapid diffusion relaxation it should be $(T_1^{1,2,3})^{1/2} \sim H_0$. Obviously the data presented in Fig. 2 show that the square root scaling of the relaxation times shows proportionality to the magnetic field with much better accuracy than the second power scaling. Therefore, as well as in the orientation-dependent relaxation investigations the results favor the rapid diffusion relaxation mechanism. Nevertheless, it does not exclude the possibility that simultaneously small amounts of the impurities lead nuclear relaxation due to the diffusion-limited relaxation mechanism, which are beyond the accuracy of the experiment.

EXPERIMENTAL STUDIES OF THE TEMPERATURE-DEPENDENT T_1 AND DISCUSSION

Temperature-dependent measurements have been carried out with the 300-MHz spectrometer. The range of temperatures, which is allowed for the goniometer probehead used in these experiments, is from 200 to 400 K. In order to ensure the validity of results, experiments on the nuclear magnetization recovery have been performed twice at each given temperature. Since there is no influence of the crystal orientation on the spin-lattice relaxation the data presented below were obtained at the magic angle orientation $B_{0\parallel}[100]$.

The behavior of the temperature dependent spin-lattice

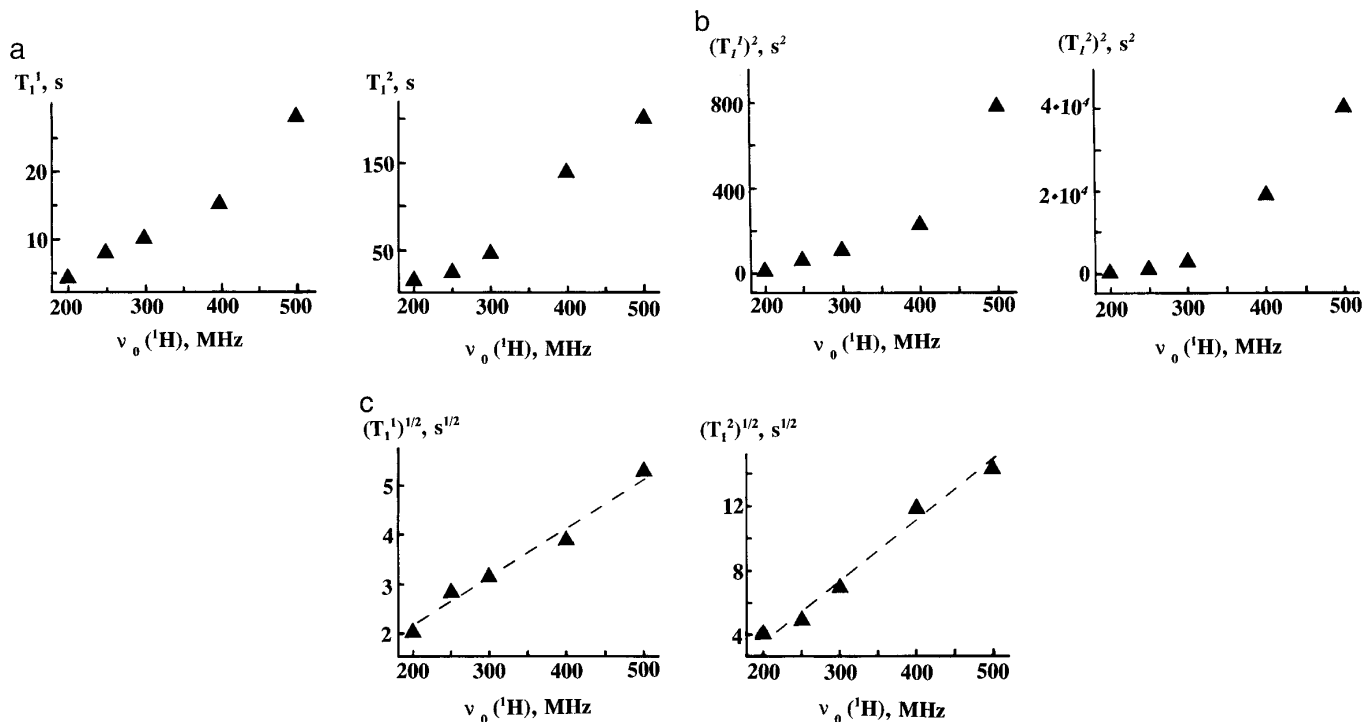


FIG. 2. Dependence of the relaxation time components (a) T_1^1 , T_1^2 , (b) $(T_1^1)^2$, $(T_1^2)^2$, and (c) $(T_1^1)^{1/2}$, $(T_1^2)^{1/2}$ on the magnetic field.

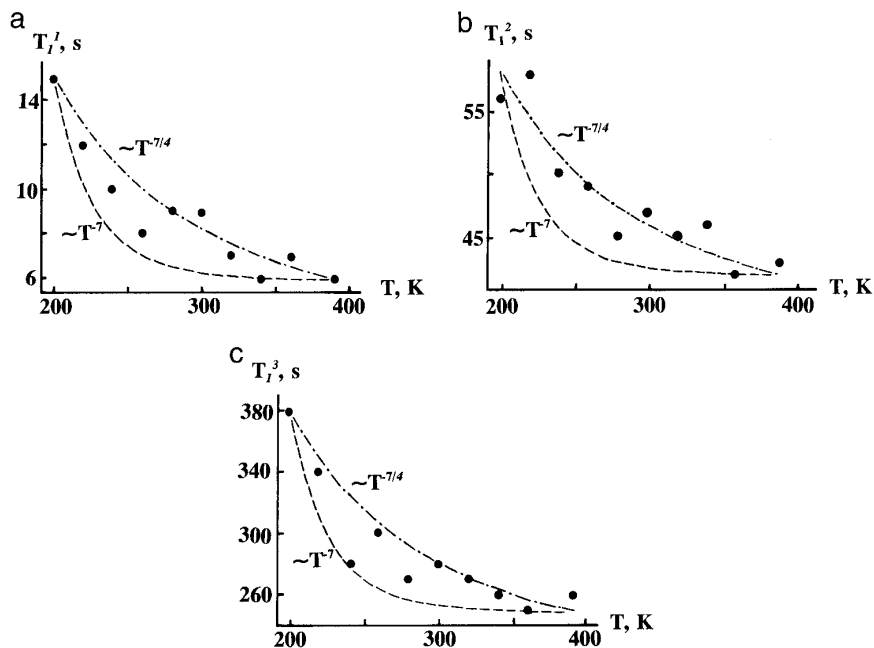


FIG. 3. Dependence of the spin-lattice relaxation time components (a) T_1^1 , (b) T_1^2 , and (c) T_1^3 on temperature.

relaxation cannot be precisely predicted from Eq. [9] for the temperature range considered (the condition $T/\Theta \leq 0.02$ is not fulfilled for our case). Nevertheless it is interesting to compare the experimental results with this theoretical approximation.

For the diffusion-limited relaxation the theory gives $T_1^i \sim T^{-N}$ ($\frac{2}{4} \leq N \leq \frac{7}{4}$), and the rapid diffusion relaxation mechanism gives $T_1^i \sim T^{-K}$ ($2 \leq K \leq 7$).

The temperature-dependent experimental points for the three components of the spin-lattice relaxation time as well as the simulating curves showing T^{-7} and $T^{-7/4}$ behaviors are presented in Fig. 3. First of all it should be noticed that all the three components of the spin-lattice relaxation time are increasing as the temperature decreases. Unfortunately, due to about 10% accuracy of the resolution of the relaxation time components and due to the relatively small temperature range allowed for the experiments (200–400 K) it is not possible to make a conclusion about the type of temperature dependence obtained experimentally: the experimental points for each relaxation time component can be fitted to temperature dependencies from T^{-7} to $T^{-3/2}$ with nearly the same approximation error. However, taking into account that the temperature behavior of the relaxation time should be weaker and closer to the stronger power (-7 or $-\frac{7}{4}$) of the temperature, the fitting dependencies are statistically more in agreement with $T_1^i \sim T^{-K}$ ($K \leq 7$) than with $T_1^i \sim T^{-N}$ ($N \leq \frac{7}{4}$). Therefore, from the temperature-dependent nuclear magnetization recovery experiments it is more probable that the rapid spin diffusion mechanism of nuclear impurity spin-lattice relaxation takes place.

CONCLUSIONS

The main results presented in the paper are the following. The multiexponential behavior of nuclear magnetization saturation recovery was observed in the ^{13}C diamond. The experimental dependencies of the nuclear spin-lattice relaxation time as a function of crystal orientation, magnetic field, and temperature were investigated. No significant influence of the diamond orientation on the nuclear spin-lattice relaxation processes was found. The field dependence of the spin-lattice relaxation time was found to be proportional to the second power of the magnetic field. The temperature investigations showed increasing spin-lattice relaxation time with decreasing temperature.

The experimental results obtained were found to correspond to the theory of relaxation via paramagnetic centers, which exhibits two possible mechanisms: the diffusion-limited relaxation and the rapid diffusion relaxation. By estimating the characteristic behaviors of the relaxation times for the diamond as functions of orientation, magnetic field, and temperature and comparing the theoretical predictions with the experimental data for the both mechanisms it was shown that the rapid diffusion mechanism plays a major role in the impurity spin-lattice relaxation processes in the ^{13}C diamond.

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