

Nuclear spin-lattice relaxation of dilute spins in semiconducting diamond

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Absorption line shape and spin-lattice relaxation-time measurements have been made on ^{13}C nuclei (1.1% abundant) in a type-IIb single-crystal semiconducting diamond. The line shape measurements are consistent with theoretical predictions for a dilute spin system. Over the temperature range 295–375 K, the spin-lattice relaxation time is long (3–4 h) and shows a temperature dependence which may be explained by means of a model in which spin diffusion plays a role, and the paramagnetic acceptor centers relax via an Orbach-type process involving excited states near the valence band.

I. INTRODUCTION

The observation of natural abundance (1.1%) ^{13}C nuclear magnetic resonance (NMR) signals in diamond has been reported by a number of workers. Retcofsky and Friedel¹ measured the chemical shift for a sample consisting of a number of gem-quality diamonds and found that the linewidth was less than 400 Hz, the limit set by instrumental broadening in their spectrometer. Wilkie, Ehlert, and Haworth² observed a broader resonance with two peaks, both in gem quality and in industrial diamonds. Spin-lattice relaxation times were found to be very long, of the order of days. In more recent work Henrichs *et al.*³ have observed a single narrow ^{13}C signal with a width of about 250 Hz in gem-quality diamonds. Broader lines were found in industrial diamond powder which were attributed to paramagnetic centers and possibly also ferromagnetic inclusions.

Duijvestijn *et al.*⁴ have shown that dynamic nuclear polarization methods may be used to detect the ^{13}C resonance in diamonds containing paramagnetic impurities (type-I diamonds). They also found that spin-diffusion effects were negligible in the spin-lattice relaxation of diamonds containing a high concentration of paramagnetic centers ($\sim 10^{19} \text{ cm}^{-3}$). Similar findings on relaxation were reported by Henrichs *et al.*³ who showed that for long times the magnetization recovered as $\exp[-(t/T_1)^{1/2}]$ in agreement with the general result given by Tse and Hartmann.⁵ A great deal of ^{13}C NMR work has been carried out on solid hydrocarbons in recent years. Cross relaxation between different spin species has been studied and further details can be found, for example, in the papers of VanderHart and Garroway⁶ and Quiraga and Virlet.⁷

No previous NMR measurements appear to have been carried out on semiconducting diamond. Diamonds of this type (IIb) are known to contain boron acceptor centers with a concentration typically in the range 10^{16} – 10^{17} cm^{-3} . A number of workers^{8–11} have exam-

ined the electrical and optical properties of IIb diamonds and the acceptor-center activation energy has been found to be 0.36 eV.

Electron spin resonance (ESR) investigations of the diamond acceptor centers have not been carried out because valence-band degeneracy effects give rise to a very large linewidth. Such effects are also important in silicon where it has been shown¹² that the application of uniaxial stress lifts the degeneracy allowing ESR spectra to be recorded.

The present investigation has involved ^{13}C NMR measurements on a type-IIb diamond with the objective of determining whether the method will prove useful in studying the acceptor centers in systems of this kind. A subsidiary objective has been the investigation of spin-diffusion effects in a dilute spin system.

II. EXPERIMENTAL DETAILS

The diamond samples were made available by the De Beers Diamond Research Laboratory. Most of the present work was carried out on a large uncut type-IIb diamond which has a mass of 6.2 carats (3.1 g) and an acceptor center concentration of approximately $3 \times 10^{16} \text{ cm}^{-3}$. ESR measurements showed that the sample had a concentration of detectable paramagnetic centers $< 10^{15} \text{ cm}^{-3}$. Some NMR measurements were made, for comparison purposes, on a 3-carat type-IIa diamond which had a very low level ($< 10^{15} \text{ cm}^{-3}$) of paramagnetic impurity centers including boron acceptor centers.

Measurements were carried out using a Bruker CXP 200 high-power NMR spectrometer operating at a frequency of 50 MHz, for the ^{13}C resonance, in a field of 4.7 T provided by a cryomagnet. Variable sample temperatures in the range 290–370 °C were obtained with a Bruker gas-flow probe.

Spin-lattice relaxation times were measured using a saturation $90^\circ \text{ comb} - \tau - 90^\circ$ pulse sequence. Typically 2 signals were averaged for each τ value and because of the

long T_1 values which were found (3–4 h) a single T_1 measurement took several days.

Absorption spectra were obtained by Fourier transforming the free induction decay (FID) signal using the on-line Bruker computer system. The broadening of the spectra due to the magnetic field inhomogeneity over the sample was estimated to be less than 75 Hz.

III. LINE SHAPE OF THE ABSORPTION SPECTRUM

The line shape of the type-IIb diamond obtained by Fourier-transforming the averaged FID signal with H_0 approximately along the [014] direction is shown in Fig. 1. The half-width at half intensity δ , corrected for the broadening due to the field inhomogeneity, is 100 Hz which is roughly the same as the value reported by Henrichs *et al.*³ The ^{13}C spins form a dilute magnetic system for which it is possible to calculate the dipolar second moment of the absorption spectrum using the Van Vleck expression^{13,14}

$$M_2 = \frac{3}{4}\gamma^4\hbar^2 I(I+1)f \sum_k \frac{(1-3\cos^2\theta_{jk})^2}{r_{jk}^6}. \quad (1)$$

In the present case γ is the ^{13}C magnetogyric ratio $I = \frac{1}{2}$, and f is the fraction of lattice sites occupied by

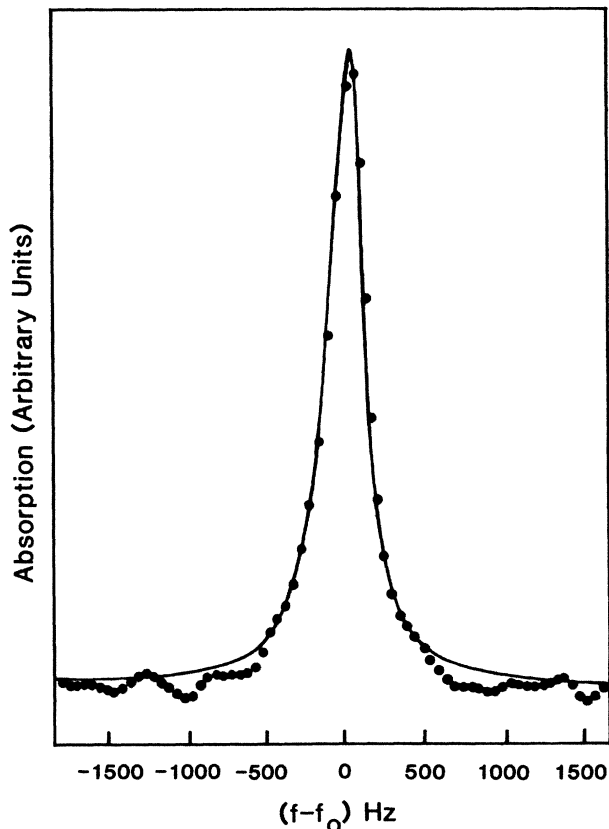


FIG. 1. Observed ^{13}C absorption spectrum in type-IIb diamond obtained by Fourier transforming the free induction decay signals obtained with H_0 approximately parallel to the [014] crystal direction. The fitted curve has a Lorentzian shape with half intensity halfwidth $\delta = 100$ Hz.

magnetic spins which is 0.011 for the ^{13}C isotope. θ_{jk} is the angle the internuclear vector r_{jk} makes with the applied field H_0 . The summation for a single crystal over all neighbors within a radius of 10 Å and with H_0 parallel to the [014] direction yields $M_2 = 0.032 \text{ G}^2$. For powdered diamond $M_2 = 0.093 \text{ G}^2$.

In a magnetically dilute system ($f \ll 0.01$) the half-intensity linewidth tends to the value

$$\delta = \frac{\pi}{2\sqrt{3}}(M_2^2/M_4)^{1/2}\sqrt{M_2}, \quad (2)$$

where M_4 is the fourth moment. The ratio M_2^2/M_4 for the diamond lattice may be estimated to be ≤ 0.05 on the basis of the result given for a simple cubic lattice¹⁴ and it follows¹⁴ that the absorption spectrum should have a truncated Lorentzian form. Figure 1 shows that the observed line shape may be represented quite well by this form. The experimental second moment is 0.036 G^2 , in good agreement with the calculated value of 0.032 G^2 for this orientation.

It may be concluded that the line shape in diamond is due to the dipolar couplings between the ^{13}C spins. The truncated Lorentzian form is consistent with what is to be expected for a dilute spin system with an f value of 0.011.

IV. RELAXATION BEHAVIOR

A representative magnetization recovery curve for the IIb diamond is shown in Fig. 2. Within the experimental uncertainty relaxation appears to be governed by a single exponential of the form $\exp(-\tau/T_1)$ over the range of τ values used.

Figure 3 shows measured T_1 values plotted against $1/T$ for the IIb diamond between 290 and 370 K. The linear form of this plot suggests that relaxation involves a thermally activated process with an apparent activation energy of 0.038 eV. T_1 measurements on the type-IIa diamond gave values at least an order of magnitude longer than those found in the IIb diamond. This suggests that the boron acceptor centers play a central role in the relaxation process.

Of the various possible spin-lattice relaxation mechanisms which may be important only two appear worthy of serious consideration. These are relaxation due to the fixed dilute system of paramagnetic trapped holes at acceptor center sites and relaxation due to the scattering of mobile holes in the valence band. Formally this may be expressed as follows:

$$1/T_1 = 1/T_1^c + 1/T_1^p, \quad (3)$$

where $1/T_1^c$ is the spin-lattice relaxation rate due to the delocalized carriers and $1/T_1^p$ is the relaxation rate produced by fixed paramagnetic centers. In Eq. (3) it is assumed that relaxation proceeds independently via the two mechanisms.

Shulman and Wyluda¹⁵ have studied spin-lattice for ^{29}Si in *n*- and *p*-type silicon as a function of mobile carrier concentration. They give an expression for the relaxation rate which has been modified in a minor way by Abraham¹⁴

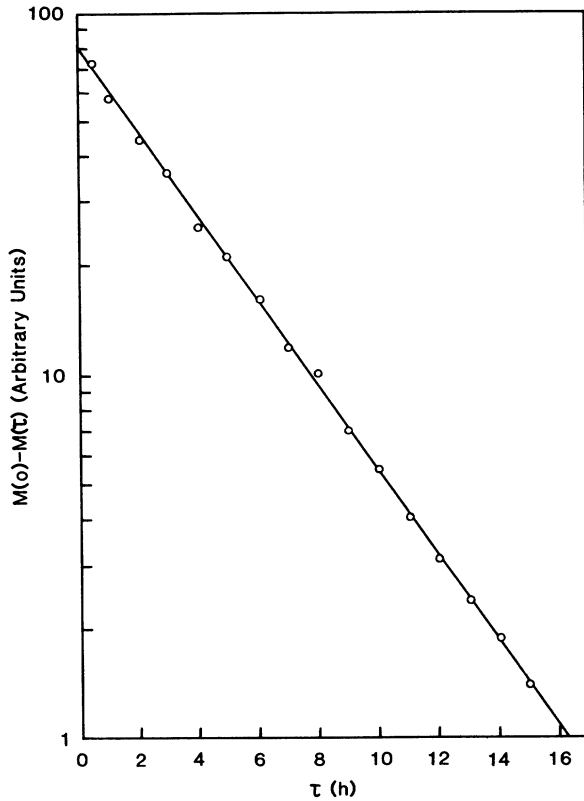


FIG. 2. Magnetization recovery curve at 335 K for ^{13}C in a IIb diamond following a saturating pulse sequence. The fitted curve represents a single exponential of the form $\exp(-\tau/T_1)$.

$$\frac{1}{T_1^c} = \frac{32}{9} \gamma_S^2 \gamma_I^2 N l \eta^2 (2\pi m_1 m_2 m_3 kT)^{1/2}. \quad (4)$$

γ_S and γ_I are the magnetogyric ratios of the electron and nuclear spins, N is the density of mobile carriers, l is the number of equivalent minima in the band, and m_1 , m_2 , and m_3 are the anisotropic effective masses. $\eta^2 = |\phi_E(0)|^2$ is the normalized density at the nucleus for a carrier of energy E .

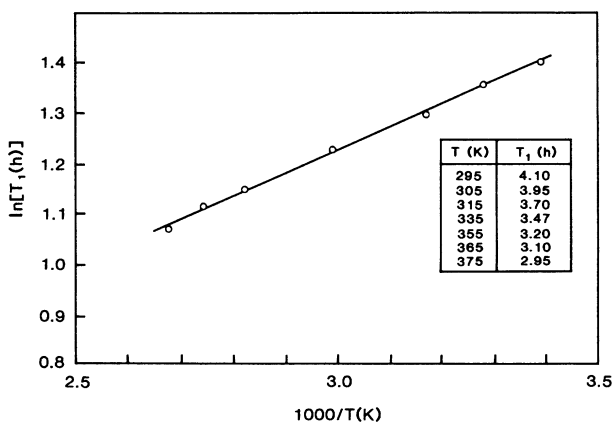


FIG. 3. Measured ^{13}C spin-lattice relaxation times T_1 in IIb diamond vs inverse temperature $1000/T$. The fitted curve is discussed in the text.

Semiconducting diamond is a p -type material and because of the purely p nature of the hole wave functions the quantity η^2 may be expected to be comparatively small and probably smaller than in p -type silicon. From the data of Dean, Lightowers, and Wight¹⁰ the hole concentration in our case may be expected to be $\sim 10^{14} \text{ cm}^{-3}$ at 300 K rising to 10^{16} cm^{-3} at 500 K. (These figures are for a diamond comparable to the one used in the present experiments, and they include the effects of partial compensation $\sim 10\%$ from donor levels higher in the gap.) For p -type silicon Shulman and Wyluda¹⁵ found that a mobile carrier density of 10^{17} cm^{-3} produced a T_1 of 150 minutes for ^{29}Si . The measured T_1 values for the IIb diamond are in the range 180–250 min. As the carrier density is much lower than in silicon and all of the other quantities in Eq. (4) are comparable for the two systems, it appears most unlikely that mobile carriers are making a detectable contribution to the relaxation rate over the temperature range involved in the present experiments. Relaxation is thus very probably due to fixed paramagnetic impurities.

Abraham¹⁴ and Goldman¹⁶ have reviewed much of the work that has been carried out related to relaxation by paramagnetic impurities. Spin diffusion plays a vital role in transferring magnetization within the spin system. For certain conditions, which are discussed below, the following expression for the relaxation rate is obtained

$$\frac{1}{T_1^p} \approx \frac{8\pi}{3} N C^{1/4} D^{3/4}, \quad (5)$$

where N is the density of electronic spins

$$C = \frac{2}{5} \hbar^2 \gamma_S^2 \gamma_I^2 S(S+1) \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} \quad (6)$$

and

$$D = \frac{1}{30} \sqrt{M_2} a^2. \quad (7)$$

D is the spin-diffusion coefficient which may be calculated using the second-moment value M_2 and the internuclear spacing a , γ_S , and γ_I have been defined previously, and S is the electron spin. In the above expression for C it is assumed that the paramagnetic-impurity spin autocorrelation function has an exponentially decaying time dependence and τ may be identified with the spin-lattice relaxation time T_{1S} of the electronic spin. Angular dependences have been ignored in the spirit of an order of magnitude calculation.

In calculating the spin diffusion constant D , allowance must be made for the fact that the ^{13}C spins are distributed in a random way in the lattice. A typical distance between two spins may be obtained using the Poisson distribution by putting the probability, $\exp[-(4\pi n_C r^3/3)]$ of finding no other spins within a distance r of a spin placed at the origin, equal to $\frac{1}{2}$. This gives $r = 0.55 n_C^{-1/3}$ which for ^{13}C in the diamond structure yields $r = 4.42 \text{ \AA}$. Using the second moment value $M_2 = 1.43 \times 10^6 \text{ (rad sec}^{-1})^2$ calculated in Sec. III gives $D \approx 7.6 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$. The distance over which the spin diffusion can operate is $L \sim \sqrt{2DT_1}$ which for $T_1 \sim 10^4 \text{ s}$ is 3900 \AA . The mean spacing between boron acceptor centers is R

$\approx 0.55n_B^{-1/3}$, which for $n_B = 3 \times 10^{16} \text{ cm}^{-3}$ gives $R \sim 180 \text{ \AA}$. Spin diffusion can thus easily transfer magnetization throughout the ^{13}C spin system during the relaxation process.

The magnitude of the correlation time $\tau_c (= T_{1S})$ in Eq. (6) is not known. As T_1 is decreasing with temperature we choose $\omega_0\tau_c > 1$ (i.e., $\tau_c > 3 \times 10^{-9} \text{ s}$) and this gives

$$\frac{1}{T_1^p} \approx \frac{8\pi}{3} ND^{3/4} \left[\frac{2}{3} \hbar^2 \gamma_S^2 S(S+1) \right]^{1/4} H_0^{-1/2} \tau_c^{-1/4}. \quad (8)$$

Comparison with experiment suggests $\tau_c \sim 10^{-4} \text{ s}$ at 300 K with a relatively large uncertainty. This value is not unreasonable (although perhaps somewhat longer than might have been expected) and this lends support to the suggested relaxation mechanism.

In the theory of spin-lattice relaxation due to fixed paramagnetic impurities a number of lengths play an important role. Two of these, the mean spacing between impurity centers R and the diffusion length L during a relaxation period, have already been discussed. Two others which deserve attention are (i) the distance $b \sim (C/D)^{1/4}$ at which spin diffusion becomes more important than direct relaxation,¹⁶ and (ii) the diffusion barrier b_0 which gives a measure of the distance over which the nuclear spins experience such a large local field due to a nearby paramagnetic impurity that they are decoupled from other nuclei and do not participate in the spin diffusion process.^{14,16} Khutsishvili¹⁷ gives the following expressions for b_0 :

$$b_0 \approx \left(\frac{\gamma_S}{\gamma_I} \right)^\alpha a \quad \text{when } \tau_c > T_2 \text{ or } \gamma_S \hbar H_0 > 2kT,$$

or

$$b_0 = \left(\frac{\gamma_S^2 \hbar H_0}{\gamma_I 2kT} \right)^\alpha a \quad \text{when } \tau_c < T_2 \text{ and } \gamma_S \hbar H_0 < 2kT.$$

In these expressions a is the nearest-neighbor spin separation and $\frac{1}{4} < \alpha < \frac{1}{3}$. At the temperatures used with the chosen magnetic field $\gamma_S \hbar H_0 < 2kT$.

Rorschach¹⁸ has given a criterion for distinguishing between the fast and slow diffusion cases in terms of the dimensionless ratio $\beta = b^2/2b_0^2$. For slow diffusion we require $\beta > 1$. The quantity b can be estimated using the expressions for C and D given above and by assuming $\tau_c \sim 10^{-4} \text{ s}$ to 10^{-6} s . In calculating b_0 it is necessary to compare the correlation time of the fluctuating local field, due to the paramagnetic impurity, with the inverse nuclear linewidth. In the present case $\tau \ll T_2 \sim 1/\delta$ and the average value of the local field rather than the instantaneous value should be used. This introduces the factor $(\gamma_S \hbar H_0/2kT)^\alpha$ into the expression for b_0 . Calculations suggest $\beta \sim 1$ and that the slow diffusion criterion is not well satisfied. The situation is complicated by the fact that spin diffusion is occurring in a very dilute random nuclear spin system. Our estimate of D is thus not really reliable. We shall assume that the system can be described in the slow diffusion limit but cannot exclude the possibility that the system is intermediate between the

slow and fast cases.

The observed temperature dependence of T_1 must now be explained. If it is assumed that the paramagnetic center spin-lattice relaxation time obeys a simple activation law $\tau_c \propto \exp(\Delta/kT)$, where Δ is an activation energy, then

$$T_1^p \propto (e^{\Delta/kT})^{1/4}. \quad (9)$$

The slope of the plot of $\ln T_1$ against $1/T$ shown in Fig. 3 is thus predicted to be $\Delta/4$. [This follows for slow diffusion from Eq. (5). For fast diffusion the slope would be Δ .] The best fit straight line through the experimental points gives $\Delta/4 = 0.038 \text{ eV}$ corresponding to $\Delta = 0.15 \text{ eV}$. It is worth noting that this is roughly half of the accepted value of the ionization energy of the boron acceptor center (0.36 eV).

The spin-lattice relaxation mechanism for the paramagnetic acceptor centers does not necessarily involve thermal excitation of the hole into the valence band. Orbach-type processes¹⁹ involving excitation to nearby energy levels may be important. Assuming a hydrogenic model for the acceptor center gives a series of excited states with energies $\epsilon_0/2^2, \epsilon_0/3^2, \dots$ above the valence band, where $\epsilon_0 = \epsilon_a - \epsilon_v$ is the energy required to excite a hole into the valence band. It should be borne in mind that unlike the case of silicon the hydrogenic model is not particularly good for diamond. (The "Bohr radius" for the ground state of the acceptor center is $r_0 \sim 3.5 \text{ \AA}$ which is comparable to the lattice constant.) It appears likely that the acceptor center spin-lattice relaxation process in diamond involves phonon excitation from the upper Zeeman level of the ground state to a nearby excited state and subsequent deexcitation to the lower Zeeman level of the ground state. Such processes may be expected to be much more effective than, say, the Raman two-phonon process mediated by spin-orbit couplings in diamond. A log-log plot of $1/T_1$ versus T is roughly linear but gives a slope of 1.4 which is not consistent with a one-phonon or two-phonon process.

Sapoval and Lepine²⁰ have studied ^{29}Si spin-lattice relaxation in high-purity silicon and have found a decrease in the relaxation rate with temperature in the range 200 to 600 K. They attribute relaxation to localized paramagnetic impurities with spin diffusion occurring in the dilute ^{29}Si system. The nature of the paramagnetic impurities in the system was not established.

On the basis of the small field dependence of T_1 and the observed temperature dependence, Sapoval and Lepine²⁰ suggest that $\omega\tau_c \gg 1$ with τ_c , as before, the electron correlation time. They further suggest the possibility that the impurity centers are paramagnetic only in their excited states in order to explain the thermally activated T_1 behavior which they found. Their data can be represented by the empirical formula

$$1/T_1 = \lambda \exp(-W/kT) \quad \text{with } W \approx 0.07 \text{ eV}.$$

An alternative explanation for their results can be given along lines similar to those advanced for the present work on diamond provided τ_c is allowed to be field dependent of the form $\tau_c \propto 1/B^n$ with $n \approx 2$. This removes the re-

quirement that $\omega\tau_c \ll 1$ and allows $T_1 \propto \tau^m$ with $m = 1$ or $\frac{1}{4}$ depending on whether the fast or slow diffusion limit applies. (Sapoval and Lepine²⁰ suggest that the slow diffusion limit applies but the evidence is not compelling in that they have not allowed for the possibility that hyperfine couplings are important in determining the radius of the diffusion barrier b_0 .) Returning to the possible field dependence of τ_c we note that Feher and Gere²¹ and Honig and Stupp²² have found a marked field dependence for the electron spin-lattice relaxation time in dilute Si:P. The field dependence is believed to result from spin-orbit coupling effects. If τ_c can be identified with the unpaired electron spin-lattice relaxation time, then the model of localized paramagnetic centers relaxing via an Orbach process could also be used to explain the data of Sapoval and Lepine.²⁰ The activation energy of 0.07 eV which they find would be related to the activation energy, to an excited state, of the impurity center in their silicon sample.

Measurements of the ¹³C T_1 made over a wider temperature range might help in understanding the paramagnetic hole relaxation processes in diamond in more detail. Alternatively and more directly, it would be of interest to attempt ESR measurements on the acceptor centers with a diamond under uniaxial stress in order to lift the valence band degeneracy. Such experiments could test the proposed relaxation mechanism.

Finally it should be noted that a number of assumptions are involved in obtaining the expression for T_1 . For example, the form chosen for the spectral density of the local field fluctuations may not be correct. The field dependence of T_1 would be helpful in testing such assumptions.

V. CONCLUSION

Measurements have been carried out involving ¹³C NMR on a type-IIb semiconducting diamond. The absorption line shape has been found to have a truncated Lorentzian form and calculations show that dipole-dipole interactions between the dilute spins (1.1% natural abundance) are responsible for the observed shape.

Spin-lattice relaxation time measurements for the ¹³C nuclei over a limited temperature range (290–370 K) have revealed the existence of a thermally activated relaxation process for the fixed paramagnetic hole centers which couple to the nuclear spins. It is suggested that this may be an Orbach-type process involving an excited state of the impurity center 0.15 eV above the ground state. Mobile holes which have a fairly low concentration ($\sim 10^{14}$ cm⁻³ at 300 K) are not believed to play a significant role in nuclear relaxation. Spin-diffusion effects have been considered and are believed to be important in transferring magnetization within the nuclear spin system during the nuclear relaxation process.

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