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NMR spectra of pure ^{13}C diamond

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NMR measurements on single crystals of pure ^{13}C diamond are reported. The line shape is very sensitive to the orientation of the external magnetic field relative to the crystallographic axes, typical of dipolar line broadening. With the magnetic field oriented along the [110] direction, the line is broad and flat, whereas a more narrow, Gaussian shape is seen along [001]. For the [111] direction, a spectacular line splitting of 8.5 kHz is observed. For the sample studied, the spin-lattice relaxation time was about 15 s at room temperature and 140 s at 140 K. The spectra are interpreted by a simple model using dipolar interactions.

I. INTRODUCTION

Already during the first years of nuclear magnetic resonance (NMR), the effects of magnetic dipolar interactions became recognized and essentially understood. Van Vleck, in a famous paper from 1948,[1] demonstrated how the width of resonance lines broadened by the dipolar interaction could be predicted by the method of moments. His method was immediately applied to the resonance of ^{19}F nuclei in single crystals of CaF_2.[2] In these crystals, the ^{19}F nuclei (nuclear spin $I = \frac{1}{2}$) form a simple cubic lattice, and due to the anisotropy of the dipolar interaction, widely different line widths are observed when the orientation of the external magnetic field is varied relative to the crystal axes. This system was later subject to more accurate studies[3] and may now be considered the classical textbook example[4] of dipolar broadening.

A simpler situation arises when the nuclear spin considered has only a few nuclear spins near enough to cause a substantial interaction. The fine structure produced in this case was observed by Pake[5] in a study of the proton resonance in gypsum, $CaSO_4{\cdot}2H_2O$. Here, the two protons in each water molecule form a pair, which is only weakly affected by other, more distant, protons. The resonance is split into two lines, a "Pake's doublet," for each pair. The splitting and its dependence on field direction allowed Pake to determine length and orientation of the proton-proton vector of the pairs. Up to now this effect has only been observed in connection with molecules.

Prediction of the precise NMR line shape to be expected for an actual system requires, in principle, knowledge of all the Van Vleck moments: the second, the fourth, etc., or some other scheme for a microscopic calculation. One of the attempts to circumvent these calculational difficulties was done by Parker and Lado,[6] who used a memory function approach taking as input the second and the fourth moment plus some less transparent qualitative knowledge of the spectrum. Among other cases, they considered the broadening of the components of a Pake's doublet as the spin pairs are brought closer together, and make the following statement: "when the spins become more or less uniformly distributed in space the resonance line becomes a single broad line as is observed from calcium fluoride."

In the following we describe NMR studies of diamonds of ^{13}C, which must be considered an ideal system for the study of nuclear magnetic dipolar interactions: ^{13}C has a nuclear spin $I = \frac{1}{2}$, so the nuclei have no electric quadrupolar moment; the material is perfectly insulating, so there are no conduction electrons, which could otherwise lead to an indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction. Therefore, such a diamond is expected to have its intrinsic NMR properties determined purely by the magnetic nuclear dipole-dipole interaction. In addition, only one nuclear species is present and all spins are positioned on equivalent crystal sites.

We find that in this system of nuclear spins with $I = \frac{1}{2}$, arranged in the diamond lattice, the two dipolar effects combine in a spectacular manner: the linewidth varies with orientation, and around particular field directions a splitting similar to a Pake's doublet is observed. The data can be understood qualitatively by means of a rather simple model. These properties make ^{13}C diamond a NMR model system exhibiting, in a very illustrative way, the effects of nuclear dipole-dipole interactions.

Seen more generally, diamond has always been one

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of the model systems for solid state physics. In the past few years, our understanding of the extreme properties of diamond has become deepened by observation of their dependence on isotopic composition. Natural carbon contains about 1.1% ^{13}C. Anthony *et al.* have produced diamonds with this "impurity" concentration reduced to 0.1% and observed a substantial increase in thermal diffusivity.[7] In diamonds of nearly pure (99%) ^{13}C, the enhanced atomic mass means reduced zero point motion and consequently a reduced lattice parameter as observed by Holloway *et al.*;[8] this in turn leads to slightly enhanced elastic constants and Ramdas *et al.*[9] conjecture from this result that ^{13}C diamond will be the hardest material known.

II. EXPERIMENTAL METHOD

Our crystals have been produced from carbon containing over 99% ^{13}C. They were synthesized[10] at high pressure and high temperature using a Ni catalyst containing a few percent Ti. Six samples of roughly 30 mg each have been available. Optical inspection showed well developed (001) and (111) faces on most of them. They were all greenish in color and transparent, except for some small inclusions of unknown composition. The lattice constant was determined by means of the $K_{\alpha 1}$ x-ray line from Cu (0.1450 nm) selected by the [111] reflection from a germanium single crystal monochromator. Using the [004] reflection from the diamond, the lattice constant was measured to be 0.3567 nm, in agreement with the value 0.356 66 nm measured by Holloway *et al.*[8]

An introductory NMR survey at 9.4 T of all samples, indicated qualitatively the features to be described below. Since the setup for this survey did not allow adequate control of crystal orientation relative to the magnet field direction, a more systematic study of line shape versus field direction was undertaken in another spectrometer.

The line shapes shown later were measured at room temperature in a Bruker MSL300 spectrometer. The ^{13}C nuclear resonance frequency was 75.468 MHz (corresponding approximately to a 7 T field). Samples were glued by means of Apiezon T grease in a sample holder consisting of three Al_2O_3 platelets forming one half of a cube. The sample holder was mounted on a Doty goniometer probehead DSI418 that allowed rotation about specific crystal axes. The orientation of these axes was determined by optical goniometry.

Spectra were recorded as Fourier transforms of free induction decay signals following a $\pi/2$ pulse. Pulse length was 5.5 μs, and the dead time delay 2 μs. The spin-lattice relaxation time, τ_1, was found to be slightly anisotropic, ranging from 14 to 17 s. Therefore, our repetition rate was kept below 3 spectra per minute. The magnetic field was rotated in several crystal planes and spectra recorded at 4.5° intervals.

As a part of the introductory survey, τ_1 was measured at a few temperatures below ambient, ranging down to 140 K. τ_1 was determined by applying a π pulse to the nuclear system and observing the subsequent recovery of the signal.

A search for paramagnetic impurities was done by electron spin resonance (ESR). A weak signal was found corresponding to a g value of 2.032. The source was not identified, but the presence of paramagnetic centers, presumably at a ppm concentration level, is significant for the relaxation processes.

III. EXPERIMENTAL RESULTS

The characteristic spectral features could be observed by rotation of the magnetic field vector in one particular plane, the $(\bar{1}10)$ plane shown in Fig. 1. Figure 2 shows some of the resulting spectra for one crystal. For illustration, every third spectrum only, at angular intervals of 13.5°, is shown. In this way, the figure covers a substantial angular range and comes close to the principal directions indicated at right. A second crystal gave results that were identical with these within the experimental resolution.

Among the spectra in Fig. 2 three characteristic shapes are apparent. Around [110] the line has a broad, trapezoidal shape. Around [001] the line is more narrow and nearly Gaussian. For field directions around [111] the resonance is split in two Gaussian lines, each of the same width as the [001] line. The splitting is most pronounced exactly in [111] directions, and to demonstrate the consistency of this observation, the directions $[11\bar{1}]$ and $[\bar{1}\bar{1}1]$ have been included in the figure. We are not aware of a similar observation in any solid crystal consisting of like nuclear spins positioned in sites that are equivalent (except for an obvious up-down asymmetry).

In Fig. 3 we display the spin-lattice relaxation time measured at various temperatures in a field of 9.4 T. The dashed line should be considered only as a guide to the

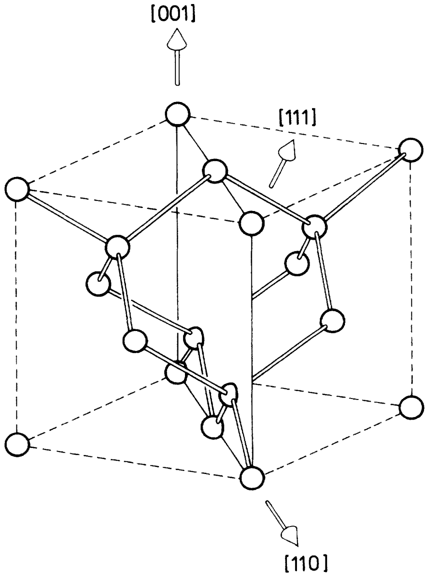

FIG. 1. Diamond lattice showing the $(1\bar{1}0)$ plane, in which the magnetic field is rotated to yield Fig. 2.

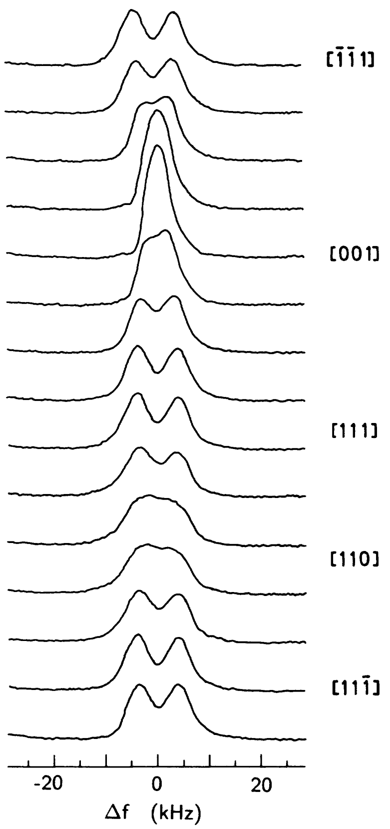

FIG. 2. A series of spectra with the magnetic field in the ($1\bar{1}0$) plane. Between each spectrum and the next the crystal is rotated 13.5° with respect to the field. During this sequence the field comes close to the crystal directions indicated at right.

eye, but it serves also to indicate the simplest *power law* that could describe the data.

IV. DISCUSSION

In a solid it is expected that all resonances are broadened by the magnetic dipole-dipole interaction

$$H_d = \frac{\mu_0}{4\pi}\gamma^2\hbar^2 \sum_{i<j} \frac{1}{r_{ij}^3} \left[\boldsymbol{I}_i \cdot \boldsymbol{I}_j - 3(\boldsymbol{I}_i \cdot \hat{\boldsymbol{r}}_{ij})(\boldsymbol{I}_j \cdot \hat{\boldsymbol{r}}_{ij})\right], \quad (1)$$

where the sum runs over all spin pairs (i,j), $\boldsymbol{r}_{ij}$ is the vector from site i to site j, and $\hat{\boldsymbol{r}}_{ij}$ is a dimensionless unit vector along $\boldsymbol{r}_{ij}$. $\gamma = 67.261$ Mrad/(s T) is the magnetogyric ratio of the ^{13}C nucleus.

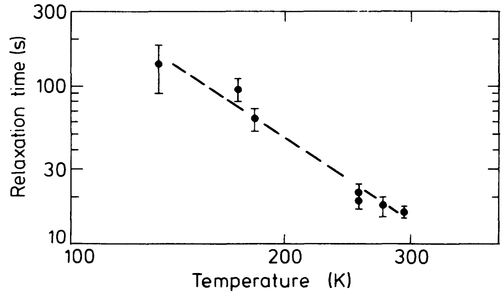

FIG. 3. Spin-lattice relaxation time at various temperatures for one sample of ^{13}C diamond, measured at 9.4 T. The dashed line, corresponding to a T^{-3} temperature dependence, only serves to illustrate how rapidly the relaxation time changes with temperature.

First we notice that the dipolar interaction is much weaker than the Zeeman interaction. Thus the only significant dipolar terms are of the types $I_i^z I_j^z$ and $I_i^+ I_j^-$ which commute with the Zeeman Hamiltonian. The truncated Hamiltonian reads

$$H_d = \frac{\mu_0}{4\pi}\gamma^2\hbar^2 \sum_{i<j} \frac{1}{r_{ij}^3}\left[I_i^z I_j^z - \tfrac{1}{4}(I_i^+ I_j^- + I_i^- I_j^+)\right] \times (1 - 3\cos^2\theta_{ij}) , \quad (2)$$

where θ_{ij} is the angle between the magnetic field direction and the vector $\boldsymbol{r}_{ij}$.

As the nuclear spin is $I = \frac{1}{2}$, no quadrupolar interaction is present, and since the diamond is an insulator, the electron mediated RKKY interaction can be ruled out as well. Furthermore all nuclear sites are equivalent, so the chemical shift is uniform and need not be considered. We will neclect the effects of impurities and discuss the observed line shapes in terms of the truncated dipolar interaction in a perfect ^{13}C diamond crystal.

a. Qualitative observations. When the applied field is along the [001] direction, all nearest-neighbor bonds are at the same angle, $\theta = 54.7°$, to the field. This is the so-called magic angle, where the term $1 - 3\cos^2\theta$ vanishes, and the truncated dipolar interaction (2) is zero. Consequently, only next-nearest neighbors and nuclei further away contribute to the dipolar line broadening. The line is thus expected to be relatively narrow, as the dipolar interaction falls off rapidly with the distance r (as $1/r^3$). This prediction is in accordance with the measured spectra, where the line is seen to have a narrow, Gaussian shape.

For the field along [110], the angles of the nearest-neighbor bonds are nonmagic, and these bonds contribute to the line broadening. The resonance is correspondingly expected to be much broader than for the [001] direction. The observed spectral line is actually rather broad and has a nearly flat top. As mentioned in the Introduction, a famous analog to these observations is the resonance of ^{19}F in CaF$_2$, where the narrow line is found for the [111] orientation and the broad, flat one at the [001] orientation, due to the simple cubic symmetry of that material.[4]

When the field is along the [111] direction, one of the four nearest-neighbor bond directions lies parallel to the field. Pairs of nuclei connected by these bonds experience the maximum truncated dipolar interaction, whereas the interaction along the other nearest-neighbor bonds is a factor of 3 smaller. This situation is very similar to that observed in gypsum, $CaSO_4{\cdot}2H_2O$, where the strong interaction between the protons in each water molecule gives rise to a triplet-singlet splitting of the energy levels, which in turn causes the line splitting known as the Pake's doublet.[5] And a doublet is indeed what we observe in ^{13}C diamond for this case.

b. Method of moments. For a more quantitative discussion of the line shapes we apply the method of moments, as developed by van Vleck.[1] The second moment, M_2, of the spectral line for a purely dipolar interaction is given rigorously[11] by

$$M_2 = \frac{\mu_0^2}{(4\pi)^2}\frac{3}{4}\gamma^4\hbar^2 I(I+1)\sum_{j\neq 0}\frac{\left(1-3\cos^2\theta_j\right)^2}{r_j^6}. \tag{3}$$

Here, an arbitrary nucleus is taken as the origin and the index j runs over all other nuclei, θ_j being the angle between the magnetic field and $\mathbf{r}_j$. Due to the strong dependence on r this sum converges rapidly, and it can be evaluated numerically. We have summed the contributions from all (2163) neighbors out to a distance of four lattice constants (about 1.4 nm), estimating the remaining contributions by an integral. In Table I the values of (3) are compared to the measured ones for the magnetic field along the three main crystal directions. Apparently, the dipolar interaction accounts for the observed anisotropy of M_2. We expect an additional broadening from (electronic) paramagnetic impurities, whose presence is signaled by the relatively short spin-lattice relaxation time. Since different broadening mechanisms yield additive components to M_2 it is noteworthy that the additional broadening of the [001] and [110] lines are clearly different. Our knowledge of the impurities is insufficient to resolve this question.

To understand the [111] line shape one must first look at the Pake's doublet splitting for an isolated pair of ^{13}C nuclei oriented with the bond parallel to the field. In terms of frequency, the splitting is given[12] by

$$2\Delta f_1 = \frac{\mu_0}{4\pi}\frac{3}{2}\frac{\gamma^2\hbar}{2\pi r_{ij}^3}\left(3\cos^2\pi - 1\right) = 6.24\ \text{kHz}. \tag{4}$$

In a diamond crystal one could assume the weaker, although not negligible, interactions between these pairs to cause a uniform Gaussian broadening (width σ_1) of the double line. For such a line shape the second moment is just

$$M_2 = \Delta f_1^2 + \sigma_1^2. \tag{5}$$

Here the first term comes from the line splitting [but is identical to the contribution to (3) coming from the neighbour in the direction of the applied field]. The Gaussian broadening

$$\sigma_1^2 = M_2 - \Delta f_1^2 = 5.17\ \text{kHz}^2 \tag{6}$$

is the sum of all other contributions to (3) but is nevertheless the smaller term.

TABLE I. The measured values of M_2 compared with the value given by the formula (3) for dipolar line broadening.

Orientation	M_2 measured (kHz^2)	M_2 calculated (kHz^2)
[001]	4.6	1.85
[110]	20.5	11.70
[111]	24.7	14.90

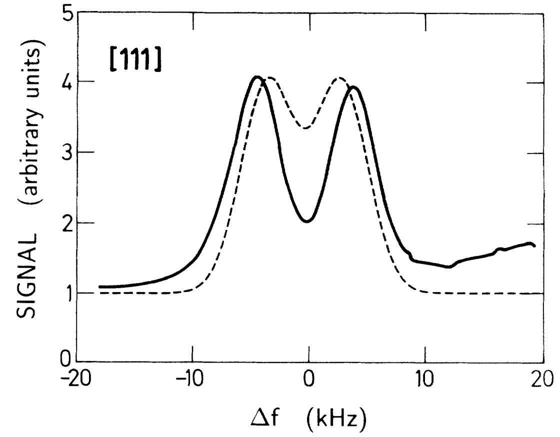

FIG. 4. A typical NMR spectrum with the magnetic field along the [111] direction. The dashed line is the line shape as calculated in our simple model assuming dipolar interactions, see text.

In Fig. 4 we show the line shape for the [111] orientation, calculated by the method described above, compared to the observed line. This curve is simply a superposition of two Gaussian lines of width σ_1 positioned $2\Delta f_1$ apart. The experimental spectrum shown nearly fits two Gaussians with $\sigma = 2.1$ kHz and $2\Delta f = 8.5$ kHz. It is evident that the measured splitting is somewhat enhanced from what is expected in the simple spin-pair picture.

c. Memory functions. A more detailed calculation of the expected line shapes may be made by considering the higher-order moments of the spectral line. The selection of line shapes having the correct values of both M_2 and M_4 has been discussed by Parker and Lado.[6] They use the approach of Gaussian memory functions as first developed by Lado, Memory, and Parker.[13] They find that the ratio M_4/M_2^2 is a natural parameter for characterizing the shape of the resonance line. Of particular interest in the present context is their analysis of what happens to an initially sharp Pake's doublet, when the two peaks of an isolated pair are broadened by spins in the neighborhood. A sharp double peak (two δ functions) corresponds to $M_4/M_2^2 = 1$, while the double-peaked shape melts into a single line for $M_4/M_2^2 = 2.85$. A single Gaussian line has $M_4/M_2^2 = 3$. For this value, Parker and Lado find a more flat-topped shape.

A significant result of the analysis is that as the ratio M_4/M_2^2 increases from 1, the peaks can move away from each other by as much as 20% . Our line shape for the [111] direction would correspond to a value near 2 for the ratio M_4/M_2^2.

d. Direct methods. The ideal way of calculating the spectral line shapes would of course be to solve the nuclear eigenvalue problem exactly. As this task is clearly impossible, a number of approximate schemes may be tried.

One of these is exact numerical diagonalizing of small clusters of spins interacting via the dipolar force. An attempt with a cluster of five spins (one spin plus four nearest neighbors) has been done by Schaumburg, Shabanova, and Sellschop,[14] who by fitting the width of the individual lines arrive at a curve very similar to the dashed line in Fig. 4.

A more interesting calculation has been performed by Rischel[15] who treated clusters of 12 spins. He finds an enhancement of the [111] line splitting that corresponds to the value observed in the present work.

An impressive agreement between observed and predicted line shapes is found in a very recent calculation by Jensen.[16] His preliminary curves fit our spectra for all three main crystal directions, although there seems to remain a discrepancy near the centers of the spectra. It should be noted that Parker and Lado[6] found a similar discrepancy in their comparison with an experimental double-peaked spectrum.

e. Spin-lattice relaxation. Compared to the day-long ^{13}C relaxation times occurring in high purity diamonds of natural carbon, the relaxation times encountered in the present work are short. Since paramagnetic impurities or at least paramagnetic centers are present, it is natural to identify the dominant τ_1 mechanism as impurity relaxation combined with spin diffusion.[17] Schaumburg, Shabanova, and Sellschop[18] compared τ_1 for a crystal from the present study with τ_1 for a purer, colorless ^{13}C diamond and came to the same conclusion, since the colorless diamond had a τ_1 of about 5 h, three orders of magnitude longer than for the greenish sample. They estimated the impurity concentration of the greenish diamond to be of the order of 1 ppm. (We have checked the colorless diamond[19] by ESR and indeed found no signal above the detection limit.)

For the relaxation mechanism mentioned, a temperature dependence is only expected for the spin-lattice relaxation of the paramagnetic impurity. The Debye temperature of diamond is around 1900 K (maybe higher for ^{13}C). In our temperature range, this relaxation rate may therefore depend on temperature T as T^7 (the prediction for Raman processes), which in turn should imply[17] a $T^{1.75}$ dependence for the nuclear relaxation rate. The stronger temperature dependence of τ_1 observed in the present work and displayed in Fig. 3 indicates a need to consider other processes as well.

V. CONCLUSION

We report NMR spectra of a pure ^{13}C diamond. The shape and broadening of the spectral lines vary with the orientation of the crystal in the magnetic field, the main feature being a line splitting observed when the field is in or near the [111] direction. The splitting and the anisotropy of the total second moment can be qualitatively understood by means of the Pake's doublet mechanism and the dipolar interaction. The size of the splitting and detailed features of line broadening and line narrowing seem to be accounted for by recent, as yet unpublished, calculations. Observed relaxation rates are not fully understood, but may be motivations for further work.

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