Zeeman and Dipolar Nuclear Relaxation by Paramagnetic Impurities in CaF_2

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The relaxation times of Zeeman and dipolar energies have been measured in a single crystal of CaF_2 containing Ce impurities at very low concentration. Measurements have been made at various temperatures between 4.2 °K and 77 °K. It is shown that the Zeeman energy relaxation passes from a rapid spin diffusion to a diffusion limited case when the temperature is increased whilst the dipolar energy relaxation seems to be diffusion limited over the whole temperature range.

1. Introduction

This work reports the relaxation behaviour of a spin system in a rigid lattice, namely that of fluorine nuclei in a calcium fluoride single crystal. It is now well established [1, 2] that if such a sample is submitted to a high external magnetic field, the energies corresponding to the Zeeman and to the truncated dipolar spin hamiltonian are well decoupled. If internal equilibrium is reached, their mean values can be desribed by two temperatures T_Z and T_D and evaluated with a density matrix which in the limit of high temperature has the form:

$$\varrho = \frac{1}{Z}\left(1 - \frac{\mathcal{H}_0}{k\,T_Z} - \frac{\mathcal{H}'}{k\,T_D}\right) \tag{1}$$

$Z = \text{Trace}\ \{1\}$ is a normalizing constant, $\mathcal{H}_0 = \sum_i - \hbar\,\gamma_I\,H_0\,I_i^Z$ is the Zeeman hamiltonian and $\mathcal{H}'$ is the Van Vleck truncated hamiltonian which commutes with $\mathcal{H}_0$.

Of course, when complete equilibrium with the lattice is realized $T_D = T_Z = T_L$ where T_L is the lattice temperature. The purpose of this work is to compare the relaxation rates of both Zeeman and dipolar subsystems, when the coupling with the lattice is achieved by the presence of a known quantity of diluted paramagnetic impurities (Ce^{+++} atoms).

We are thus in a situation where each impurity relaxes the neighbouring spins and the local changes in Zeeman or dipolar energies are spread throughout the entire crystal by a process of spin diffusion. The existence of this process ensures the existence of spin temperatures and the validity of Eq. (1) for the great majority of the spins in the crystal [3].

2. Experimental

We have investigated an "Isomet" single crystal of CaF_2 containing .001% of Ce atoms.

The measurements were performed with a home made coherent pulse spectrometer at a frequency of 15 MHz. The Zeeman relaxation time T_{1Z} was measured by first saturating the magnetization M_Z with a $\pi/2$ pulse. The recovery of M_Z was then analysed with $\pi/4$ pulses applied at different times after the first saturating pulse. In order to measure the dipolar relaxation time T_{1D} a great part of the Zeeman order was converted into dipolar order corresponding to a low value of T_D. This transfer was achieved by a method described by Jeener and coworkers [4] and has been used already by Johnson and Goldburg [5] for a similar type of measurement where the relaxation was mainly due to quadrupolar coupling. The method consists of applying a set of two pulses to the sample: a $\pi/2$ one followed by a $\pi/4$ one. The distance between them must be of the order of T_2 and their phases should be orthogonal. The system is then allowed to relax and the dipolar free induction decay is measured by applying $\pi/4$ pulses at different times after the transfer. However, the decay signal consists in general of a mixture of Zeeman and dipolar signals and these components must be separated by orthogonal phase sensitive detection as explained in a previous paper [6]. For full details about the method and the underlying theory the reader is referred to Ref. [4, 6].

Fig. 1 * shows the free induction decays corresponding to cases where the order lies almost entirely in the

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[1] A. G. Anderson and S. R. Hartmann, Phys. Rev. **128**, 2023 [1962].

[2] B. N. Provotorov, Zh. Eksperim. Teor. Fiz. **41**, 1582 [1961]; Transl. Soviet Phys. J. E. T. P. **14**, 1126 [1962].

[3] I. Solomon and J. Ezratty, Phys. Rev. **127**, 78 [1962].

[4] J. Jeener, R. Du Bois and P. Broekaert, Phys. Rev. **139**, A 1969 [1965] (see also J. Jeener and P. Broekaert, Proceedings of the 13th Colloque Ampère Louvain 1964).

[5] B. C. Johnson and W. I. Goldburg, Phys. Rev. **145**, A 380 [1965].

[6] J. Jeener, H. Eisendrath and R. Van Steenwinkel, Phys. Rev. **133**, A 478 [1964].

* Fig. 1 see p. 818 a.

R. Van Steenwinkel and P. Zegers, *Zeeman and Dipolar Nuclear Relaxation by Paramagnetic Impurities in CaF_2 (S. 818).*

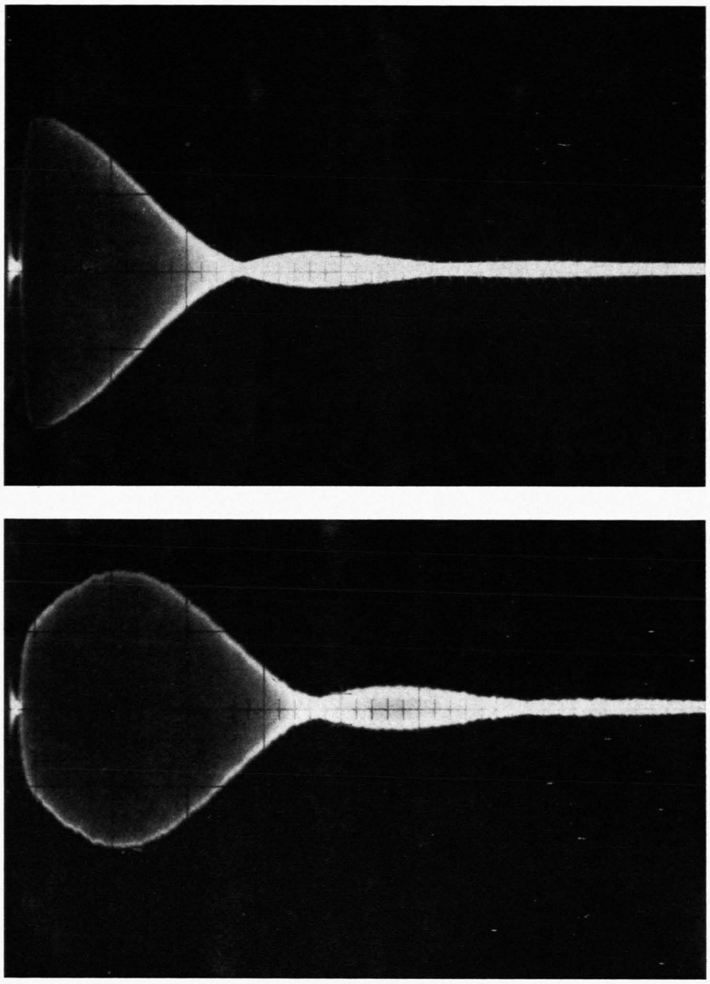

Fig. 1. High frequency free decays of Zeeman and dipolar signals in CaF_2 with H_0 in the (110) direction.

Zeeman subsystem (normal free decay) or in the dipolar subsystem. It is clear from the photograph that the derivative of the Zeeman signal is proportional to the dipolar signal as it should be [6].

The cryostat used for the experiment is a continuous flow cryostat which has a stable operation down to helium temperature. A complete description of it can be found in Ref. [7].

3. Discussion of the Experimental Results

The experimental results are presented in Fig. 2 where both $1/T_{1\mathrm{Z}}$ and $1/T_{1\mathrm{D}}$ are plotted as a function of $10^3/T$. In all the experiments, the recovery of equilibrium could be characterized by simple exponential behaviour in both subsystems. Therefore the time evolution of the spin system is characterized by the set of equations:

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\mathcal{H}'\rangle = -\frac{1}{T_{1\mathrm{D}}}\left[\langle\mathcal{H}'\rangle - \langle\mathcal{H}'\rangle_0\right] \tag{2}$$

and

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\mathcal{H}_0\rangle = -\frac{1}{T_{1\mathrm{Z}}}\left[\langle\mathcal{H}_0\rangle - \langle\mathcal{H}_0\rangle_0\right] \tag{3}$$

where the brackets $\langle\ \rangle$ indicate mean values.

Deviation from the exponential behaviour in the very beginning of the relaxation process could not be observed in our experiments even in the region of very short correlation time (diffusion limited case). This is due to our very low impurity concentration.

Since the spin lattice relaxation time of the Ce impurity in CaF_2, which is the correlation time for the nuclear relaxation (the electronic T_2 should play no role because of the very low electronic interaction specific heat), is not known for the Ce concentration we use, we will not try to give a quantitative justification of our results but rather explain them with some semi-quantitative arguments.

As shown in Ref. [3, 8] the theory for spin lattice relaxation of the magnetization in solids can be extended without difficulty to the case of relaxation of the spin-spin coupling energy. The main assumption in this connection is that spin lattice relaxation is weak enough so that the equilibrium form of Eq. (1), is not disturbed and relaxation is manifested by slow changes in T_Z or T_D [*].

The total hamiltonian of our spin system is:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' + \mathcal{H}'' + \mathcal{H}_\mathrm{L}(t) \tag{4}$$

where $\mathcal{H}_0$ is the Zeeman hamiltonian, $\mathcal{H}'$ is the secular part of nuclear dipolar interaction, $\mathcal{H}''$ is the part which does not commute with $\mathcal{H}_0$, and $\mathcal{H}_\mathrm{L}(t)$ is the nuclear-electron dipolar coupling. In (4) we have omitted the interelectronic interaction which is reasonable in view of the great dilution of the impurities.

In solids $\mathcal{H}_\mathrm{L}(t)$ can include the modulation of the dipolar as well as the scalar electron-nuclear interaction. If the relaxation time $T_{1\mathrm{S}}$ of the paramagnetic impurity is not too short the dipolar interaction is most effective as a relaxing agent because it contains terms having non zero matrix elements between functions with the same electronic state, corresponding to very small change in energy. In $\mathcal{H}_\mathrm{L}(t)$ we therefore keep only the part which does not involve an electronic flip.

$\mathcal{H}_\mathrm{L}(t)$ can then be written in the form:

$$\mathcal{H}_\mathrm{L}(t) = \sum_{i,q} \mathcal{H}_{\mathrm{L}i}^{q}(t)$$

where $q=0$ for the term in $S_\mathrm{Z} I_\mathrm{Z}$ of the electron nucleus interaction and $q=+1, -1$ respectively for terms in $S_\mathrm{Z} I^+$ and $S_\mathrm{Z} I^-$ and i characterizes one nucleus. With these definitions the relaxation times for a homogeneous relaxation can be written as:

$$\frac{1}{T_{1\mathrm{Z}}} = \frac{1}{\hbar^2 \operatorname{Trace} \mathcal{H}_0{}^2} \sum_{q \neq 0} \int_0^\infty e^{iq\omega_\mathrm{I} t} \operatorname{Trace}\{\mathcal{H}_\mathrm{L}^{q}(0), \mathcal{H}_\mathrm{L}^{-q}(t)\}, \tag{5}$$

$$\frac{1}{T_{1\mathrm{D}}} = \frac{-1}{\hbar^2 \operatorname{Trace} \mathcal{H}'^2} \left\{ \int_0^\infty \operatorname{Trace}[\mathcal{H}_\mathrm{L}^{0}(0), \mathcal{H}'] [\mathcal{H}_\mathrm{L}^{0}(t), \mathcal{H}'] \,\mathrm{d}t + \sum_{q \neq 0} \int_0^\infty \mathrm{d}t\, e^{iq\omega_\mathrm{I} t} \operatorname{Trace}[\mathcal{H}_\mathrm{L}^{q}(0), \mathcal{H}'] [\mathcal{H}_\mathrm{L}^{-q}(t), \mathcal{H}'] \right\}. \tag{6}$$

Equations (5) and (6) correspond to similar expressions derived in Ref. [5, 8].

Equations (5) and (6) are not directly applicable to relaxation by paramagnetic impurities as this relaxation is strongly inhomogeneous. However (5) can be developed for the relaxation of the mean magnetization of the i-th spin with coordinates r_i, Θ_i, φ_i with respect to the impurity. The more familiar relation (7) is then obtained (see for instance Ref. [9], Chapt. IX)

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[7] J. Haupt, Z. Angew. Phys. **23**, 377 [1967].

[8] J. Jeener, to be published in Advances in Magnetic Resonance, Academic Press N. Y.

[*] The reader is especially referred to Ref. [3] for a complete discussion of the validity of the concept of spin temperature in the case of relaxation by paramagnetic impurities.

[9] A. Abragam, The Principles of Nuclear Magnetism, Oxford at the Clarendon Press, London 1961.

$$\left(\frac{1}{T_{1Z}}\right)_i = \frac{9}{4} \cdot F^2(\Theta_i)\,\frac{\gamma_I^2\,\gamma_S^2\,\hbar^2}{r_i^6} \cdot \frac{\tau}{1+\omega_I^2\,\tau^2} \tag{7}$$

where the angular function $F(\Theta_i) = \sin\Theta_i \cos\Theta_i$.

In (7) the meaning of $(1/T_{1Z})_i$ is defined by the relation:

$$\frac{\mathrm{d}\langle I_i^Z\rangle}{\mathrm{d}t} = -\left(\frac{1}{T_{1Z}}\right)_i \{\langle I_i^Z\rangle - \langle I_i^Z\rangle_0\}\,. \tag{8}$$

In the same way, Eq. (6) can be used to compute the relaxation time for the mean dipolar energy of a pair of spins defined by the coordinates r_i, Θ_i, φ_i and r_j, Θ_j, φ_j.

$$\left(\frac{1}{T_{1D}}\right)_{ij} = \gamma_I^2\,\gamma_S^2\,\hbar^2\,\left\{\frac{1}{12}\left(\frac{f(\Theta_i)}{r_i^3} - \frac{f(\Theta_j)}{r_j^3}\right)^2 \tau + \frac{3}{8}\left(\frac{5\,F^2(\Theta_j)}{r_j^6} + \frac{8\,F(\Theta_i)\,F(\Theta_j)}{r_i^3\,r_j^3}\cos(\varphi_i - \varphi_j) + \frac{5\,F^2(\Theta_i)}{r_i^6}\right)\frac{\tau}{1+\omega_I^2\,\tau^2}\right\} \tag{9}$$

where $f(\Theta_i) = 1 - 3\cos^2\Theta_i$, and the meaning of $(1/T_{1D})_{ij}$ is defined by the relation:

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \mathcal{H}'_{ij}\rangle = -\left(\frac{1}{T_{1D}}\right)_{ij} \{\langle \mathcal{H}'_{ij}\rangle - \langle \mathcal{H}'_{ij}\rangle_0\}\,. \tag{10}$$

The relaxation times defined in (8) and (10) depend on the coordinates of the spin or of the pair of spins considered. Rate equations for the total Zeeman or dipolar energy like (2) and (3) are consequences of the existence of spin temperatures which guarantee the fact that the average value of the Zeeman energy of one spin is proportional to the total Zeeman energy and the average value of the dipolar interaction $\langle \mathcal{H}'_{ij}\rangle$ of a couple of spins is proportional to the total dipolar energy [3]. In the immediate vicinity of an impurity the direct relaxation processes are very strong and no temperature can be defined. However, De Gennes has shown (for the Zeeman case) that outside a sphere of radius a_Z spin diffusion insures the existence of one single Zeeman temperature [11]. In the same way it seems reasonable to assume that diffusion of dipolar energy will insure the existence of a single dipolar temperature outside a sphere of radius a_D surrounding the impurity. The radii a_Z and a_D are fixed by the diffusion constants and the direct relaxation rates. With these assumptions it is easily shown from (8) and (10) that the measured relaxation rates are given by:

$$\frac{1}{T_{1Z}} \sim \sum_i \left(\frac{1}{T_{1Z}}\right)_i \tag{11}$$

where the sum is extended on spins outside a sphere of radius a_Z

and
$$\frac{1}{T_{1D}} \sim \sum_{i \neq j} \left(\frac{1}{T_{1D}}\right)_{ij} \alpha_{ij} \tag{12}$$

where the sum is to be extended on spins outside a sphere of radius a_D. In (12) α_{ij} is the proportionality coefficient between $\langle \mathcal{H}'\rangle$ and $\langle \mathcal{H}'_{ij}\rangle$ as mentioned above,

$$\langle \mathcal{H}'_{ij}\rangle = \alpha_{ij}\langle \mathcal{H}'\rangle \tag{13}$$

and from the form (1) of the density matrix:

$$\alpha_{ij} = \frac{\mathrm{Trace}\,(\mathcal{H}'_{ij})^2}{\mathrm{Trace}\,(\mathcal{H}')^2}\,.$$

Let us now go back to equation (9). We simplify it by putting $\Theta_i = \Theta_j$, $\varphi_i = \varphi_j$ and averaging over the angles Θ_i:

$$\left(\frac{1}{T_{1D}}\right)_{ij} = \gamma_I^2\,\gamma_S^2\,\hbar^2\left\{\frac{1}{15}\left(\frac{1}{r_i^3} - \frac{1}{r_j^3}\right)^2 \tau + \frac{1}{20}\left(\frac{5}{r_i^6} + \frac{8}{r_i^3\,r_j^3} + \frac{5}{r_j^6}\right)\frac{\tau}{1+\omega^2\,\tau^2}\,.\right. \tag{14}$$

It is clear from (14) that if the fields at the i and j sites are equal $(r_i = r_j)$ the first term vanishes and we have

$$3\left(\frac{1}{T_{1D}}\right)_{ij} = \left(\frac{1}{T_{1Z}}\right)_i$$

a result already derived in Ref. [3]. In this case, the Zeeman and dipolar relaxation rates would be proportional to each other for any value of the correla-

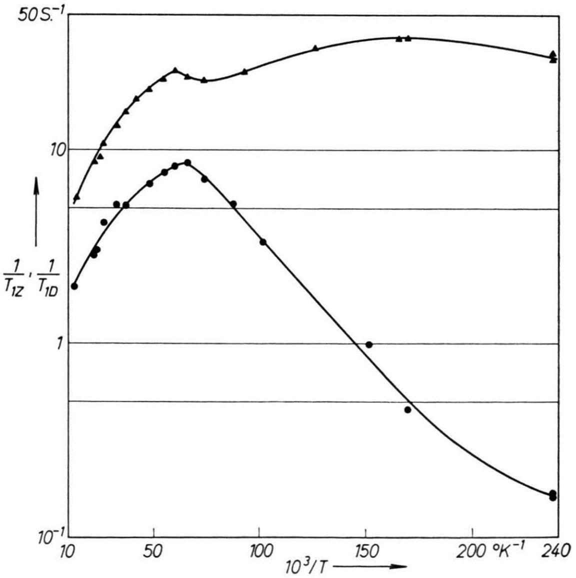

Fig. 2. The relaxation rates $1/T_{1Z}$ (●) and $1/T_{1D}$ (▲) are plotted vs. the inverse of temperature.

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[11] P. G. De Gennes, J. Phys. Chem. Solids **7**, 345 [1958].

tion time, at least in the limit of validity of the present theory [4, 8] where it is supposed that:

$$\frac{1}{\hbar}\left[\langle \mathcal{H}_{\mathrm{L}}^{2}(t)\rangle\, \tau^{2}\right]^{1/2} \ll 1 . \qquad (15)$$

This conclusion is however in contradiction to our experimental results which show a ratio of dipolar to Zeeman relaxation rate equal to 2.9 ± 0.2 only for temperatures above 17 °K. Below this point this ratio begins to increase and it reaches a maximum value of about 190 at 4.2 °K.

The increase of the dipolar relaxation rate down to 6 °K is obviously due to the presence of the first term in (9) and (14) which is simply proportional to the correlation time τ and related to the difference in local fields at sites i and j. This difference is responsable for the fact that spins i and j precess around different effective fields so that their dipolar interaction changes each time the electronic spin flips.

Since the exact temperature dependence of the electronic spin relaxation time is not known we make the reasonable hypothesis that $\tau = T_{1\mathrm{S}} = A\,T^{-n}$ and look for the coherence of the experimental results under this assumption. The result of this analysis is presented in Table 1 where we distinguish four temperature regions for which the relaxation rates have different correlation time dependence. Our experiments are best fitted for a value of n equal to 4.5. This value is unfortunately difficult to check with direct electronic relaxation measurements.

The Zeeman relaxation rate passes through a maximum at about 15 °K where, according to (7) the electron relaxation time equals the inverse nuclear frequency $\omega_{\mathrm{I}} = 84 \cdot 10^{6}\ \mathrm{sec}^{-1}$. For higher temperatures $1/T_{1\mathrm{Z}}$ depends on $\tau^{1/4}$ while for temperature between 6 °K and 12 °K it depends on $1/\tau$. This behaviour is interpreted as a passage from the high temperature diffusion limited relaxation to the rapid diffusion case [12]. We have implicitly supposed that all the temperature dependence of the relaxation time is contained in τ and not in the dimension of the diffusion barrier. This assumption is valid from 6 °K to 10 °K in view of the extreme insensitivity of the diffusion barrier to the electronic relaxation time [13]. Below 6 °K, the Zeeman relaxation rate slows down. This is probably due to the fact, that at the lowest temperature the electronic relaxation rate becomes more and more temperature independent [14].

An interesting result concerning $1/T_{1\mathrm{D}}$ is its dependence on $\tau^{1/4}$ in all the temperature regions. This means, no barrier prevents free diffusion of dipolar energy.

In the first region, $\omega_{\mathrm{I}}\,\tau < 1$, both terms of (9) are proportional to τ but the second is dominant and $1/T_{1\mathrm{D}}$ shows thus a maximum at $\tau = 1/\omega_{\mathrm{I}}$.

For $\tau > 1/\omega_{\mathrm{I}}$, the second term in (9) decreases while the first one still increases. Both give equal contributions at $\tau = \tau'$ corresponding to the minimum in the $1/T_{1\mathrm{D}}$ curve.

Finally, when $\tau > \tau'$ the dipolar relaxation rate increases due to the first term of Eq. (9).

As we saw before, Eq. (9) does not give the correct τ dependance of the relaxation time and Eq. (12) should be used. This relation is however difficult to evaluate without a theory for the diffusion of dipolar energy i. e. without the knowledge of a_{D}. However, by analogy with the Zeeman case, it is very likely that Eq. (12) is related to the power

Temperature region	$1/T_{1\mathrm{Z}}$	$1/T_{1\mathrm{D}}$	Interpretation
1 $T > 18$ °K	$\sim T^{-n/4} \sim \tau^{1/4}$	$\sim T^{-n/4} \sim \tau^{1/4}$	$\omega_{\mathrm{I}}\,\tau < 1$; Diffusion limited relaxation
2 12 °K $< T <$ 18 °K	Transition region		$\omega_{\mathrm{I}}\,\tau \sim 1$; For $T_{1\mathrm{Z}}$ transition to rapid diffusion
3 6 °K $< T <$ 12 °K	$\sim T^{n} \sim 1/\tau$	$\sim T^{-n/4} \sim \tau^{1/4}$	$\omega_{\mathrm{I}}\,\tau > 1$; $T_{1\mathrm{Z}}$: Rapid diffusion $T_{1\mathrm{D}}$: Diffusion limited relaxation
4 $T < 6$ °K	$\sim T^{n} \sim 1/\tau$	$T^{n/4} \sim \left(\frac{1}{\tau}\right)^{1/4}$	Theory of Slichter and Ailion [10]

Table 1.

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[10] C. P. Slichter and D. Ailion, Phys. Rev. **135**, A 1099 [1964].

[12] W. E. Blumberg, Phys. Rev. **119**, 79 [1960].

[13] H. E. Rorschach, Physica **30**, 38 [1964].

[14] R. W. Bierig, M. J. Weber and S. I. Warshaw, Phys. Rev. **134**, A 1504 [1964].

1/4 of τ in the various temperature regions considered. This dependence is effectively observed and can be predicted with rough arguments of comparison between the dipolar and the Zeeman case.

As a last remark we should add that Eq. (9) has been evaluated numerically taking r_i and r_j as the radii of the first and second shell of nuclei around the paramagnetic impurity. The obtained ratio of the maximum dipolar relaxation rate at $\tau = 1/\omega_{\text{I}}$, to the minimum one at $\tau = \tau'$ is 1.18, while the experimental value is 1.15.

For pairs of nuclei not involving the first shell this ratio is much higher. This shows that the important region for the dipolar relaxation lies very close to the impurity and the radius at which relaxation by spin diffusion balances direct relaxation is of the order of the first shell radius.

Finally, it should be mentioned that below 6 °K the correlation time becomes so long that condition (15) is no more valid. In the region of liquid helium and below, the relaxation will be governed essentially by the theory of SLICHTER and AILION [10] which again predicts $T_{1\text{D}}$ to be proportional to the correlation time.

4. Conclusions

Our experiment suggests strongly that the dipolar energy relaxation is always governed by diffusion whilst the Zeeman one passes at low temperature to a diffusion independent law. The transition point appears for correlation times of the order of 10^{-8} sec. The diffusion constants for Zeeman and dipolar energy are of the same order as evidenced by the high temperature measurements (see also Ref. [4]). Large differences can however be observed between both relaxation rates for correlation times longer than $1/\omega_{\text{I}}$. These are due to the effectiveness of the energy conserving part of the electron-nucleus interaction in relaxing the nuclear dipolar energy together with the fact that the Zeeman relaxation rate becomes diffusion independant.

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