Dynamic Polarization in Single Crystals of CaF$_2$ Containing H Atoms as Paramagnetic Impurities

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Formulae for dynamic polarization in solids having an inhomogeneous electron spin system and a nuclear spin system which can be described by one single spin temperature were derived. It was assumed that the spin temperature, in the rotating frame of those paramagnetic centres which fulfill $\omega_e = \omega + \omega_n$ or $\omega_e = \omega - \omega_n$, can increase due to thermal contact with the nuclear spin system brought about by high microwave power. Field fluctuations, at the positions of the paramagnetic centres, due to relaxation of surrounding nuclei and paramagnetic centres were also taken into account. Formulae obtained for the enhancement and polarization time as a function of microwave power and for the enhancement as a function of field modulation frequency and -amplitude agreed well with the experimental results in CaF$_2$ single crystals containing H atoms.

It has been reported earlier that a strong solid state effect (maximum enhancement of 190) can be observed in CaF$_2$ with diluted H atoms as paramagnetic impurities. In this preliminary work a qualitative explanation was given for both the strong solid state effect in CaF$_2$ and the fact that the enhancement could be increased by modulating the magnetic field.

In this model the nuclear spin system, where the internal equilibrium is brought about by spin diffusion, was supposed to be in thermal contact with two types of paramagnetic centres: a few polarizing centres $N_p$, which fulfill the conditions $\omega_e = \omega + \omega_n$ or $\omega_e = \omega - \omega_n$ and which are at a low rotating frame spin temperature $T_S$, created by microwave irradiation and many relaxing centres $N_r$ at lattice temperature $T_L$. The spin temperature of the nuclear spin system (it is assumed that this system can be described by one single spin temperature) will lie between $T_S$ and $T_L$, depending on the number of polarizing and relaxing centres and the thermal contacts involved.

The velocity of energy transfer between polarizing centres and the nuclear spin system increases proportionally with microwave power, while nuclear relaxation is not influenced. We would therefore expect that for sufficient microwave power the maximum value $\gamma_d/\gamma_n$ for the enhancement would be reached.

This is, in practice, rarely realized due to the fact that at a certain power level the polarizing centres receive more energy per unit time, than they can dissipate into the lattice. At this point the polarizing electrons are warmed up in the rotating frame and the enhancement becomes power independent at a value which can be much lower than $\gamma_d/\gamma_n$.

The following formula for the enhancement was obtained:

$$E = \frac{P}{P_s} = \left( \frac{N_p/n}{1/T_{1n} + 1/T_{n,exp}} \right) \cdot \left( \frac{1}{1/T_{1n} + 1/T_{n,exp}} \right) + 1/T_{1n} .$$

In Eq. (1 a)

$$1/T_{1n} = N_r \int \frac{C/r^3}{d} 2 \pi r^2 dr = \frac{\pi}{4} \pi N_r C/d^3$$

for rapid spin diffusion is the bulk nuclear relaxation rate due to the $N_r$ relaxing paramagnetic centres;

$$1/T_{1n} = n \int \frac{(s + 1)}{C/r^3} 4 \pi r^2 dr = \frac{\pi}{4} \pi n \cdot \frac{(s + 1)}{C/d^3}$$

is the inverse of the characteristic time for energy exchange between the electron in the rotating frame which fulfils $\omega_e = \omega \pm \omega_n$, and the nuclear spin system with $r > d$; $s = \gamma_d^2 H^2 T_e T_2 e$; $N_p$ = number of polarizing electrons per/cm$^3$; $n$ = number of fluorine nuclei per cm$^3$; $T_1e$ = electron spin-lattice relaxation.


time; \( C \approx \frac{8}{5} \gamma_e^2 \gamma_n^2 h^2 S(S+1) \cdot T_{1u}/(1 + \omega_n^2 T_{1u}^2) \).

\( \Pi_0 \) and \( P_0 \) are the Boltzmann polarizations for electrons and nuclei respectively.

Although this equation explains much of the experimental results, there are some discrepancies.

1. The first drawback is that the width \( \delta H \) of the polarizing region in the ESR line, related to \( N_0 \), calculated with Eq. (1 a) and the experimental value of \( E_{\text{max}} = 190 \) (\( \delta H = 0.4 \text{ Oe} \)) is much higher than one would expect theoretically (\( \delta H = 0.02 \text{ Oe} \)).

2. A second difficulty arises from the fact that the theoretical \( E - H_\perp \) curve does not coincide at all with the experimental curve. The first curve is saturated at a much lower value of the microwave power than the second one.

In fact Eq. (1 a) contains the important hypothesis that each paramagnetic centre stays permanently in a nonpolarizing or polarizing state. The magnetic field at the position of a paramagnetic centre, however, is made up of a time independent contribution plus a contribution from surrounding nuclei and paramagnetic centres, which may fluctuate due to spin-spin and spin-lattice relaxation processes.

The aforementioned discrepancies can be avoided when we take into account these local field fluctuations. In this way the strong solid state effect, the microwave power dependence of the enhancement and of the polarization time, can be described in a satisfactory way. This will be shown in the following.

1. Width \( \delta H \) of the Polarizing Region

In the model proposed in the introduction, the polarizing electrons have their Larmor frequencies in a region of the ESR line around \( \omega_e = \omega \pm \omega_n \) with width \( \delta H \). Knowledge of \( \delta H \) is essential for the calculation of the enhancement and of the polarization time and will therefore be evaluated first.

An electron will be in a polarizing state when the condition for the solid state effect is fulfilled with at least some of its surrounding nuclei. These nuclei have their Larmor frequencies spread over a certain range, the width of which determines \( \delta H \).

The nuclear Larmor frequencies \( \omega_n \) depend on the external static magnetic field \( H_0 \) and on the static part of the magnetic field induced by neighbouring nuclei and electrons. \( \omega_n \) can differ strongly from \( \gamma_n H_0 \), especially for nuclei close to paramagnetic centres. However, nuclei close to the electron, with \( r < b \) (for diffusion limited polarization) or \( d \) (for rapid spin diffusion), although in good thermal contact with the electron, are in bad thermal contact with the nuclear spin system and are for the polarization of the bulk nuclei of little importance.

The Larmor frequencies of nuclei with \( r > d \) or \( b \) which influence the polarization of the bulk nuclei lie in a frequency region around \( \gamma_n H_0 \) with a width of approximately \( \gamma_n (\Delta H + 2 \mu_e r^3) \). (\( \Delta H \) is the width of the NMR line, \( r \) is \( b \) or \( d \) and \( \mu_e \) is the magnetic moment of the electron.)

For the case of spin diffusion the width of the polarizing region in the ESR line around \( \omega_e \gamma_n = \omega \gamma_n \pm \omega_n / \gamma_n \) can be determined with the help of \( \gamma_n (\Delta H + 2 \mu_e r^3) \) and the condition for the solid state effect \( \omega_e = \omega \pm \omega_n \). One obtains

\[
\delta H = \frac{\gamma_n}{\gamma_e} (\Delta H + 2 \mu_e r^3) \quad \text{(2)}
\]

with \( r = d \) or \( b \) when \( b > d \).

With Eq. (2), for a CaF\(_2\) single crystal containing H-atoms with [110] \( \parallel H_0 \), the aforementioned value of 0.02 Oe (with \( d = 15 \text{ Å} \) and \( \Delta H = 2.5 \text{ Oe} \)) is obtained.

2. Local Field Fluctuations

Due to field fluctuations induced at the position of the paramagnetic centre by surrounding nuclei and electrons, the electron can be said to jump from one place in the ESR line to another and will sometimes have its frequency in the polarizing region (\( \delta H \)). It can happen that the electron polarizes its surrounding nuclei continuously even when it spends only a part of the time in the polarizing region. In this case the number of “polarizing” electrons \( N_0 \) will be much higher than when field fluctuations are absent. One can say that the effective width of the polarizing region increased due to field fluctuations.

We will now study the influence of field fluctuations on the width of the polarizing region for an inhomogeneous ESR line with spin packets of width \( \xi \) (we assume that spectral diffusion and cross

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7 H. E. Rorschach, Physica 30, 38 [1964].
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relaxation are absent). The field fluctuations at the position of an electron, induced by neighbouring electrons make the electron "jump" within a spin packet while on the other hand, field fluctuations induced by neighbouring nuclei make the electron jump from one spin packet (or from one ESR line) to another.

We will initially neglect field fluctuations due to neighbouring nuclei by assuming that they are very slow. The electron will then stay in the spin packet and jump within it with a characteristic time $T_{2e}$ (electron spin spin relaxation time).

When the condition for the solid state effect is fulfilled somewhere in the investigated ESR line and when $\delta H$ is smaller than $\xi$, then the polarizing region will overlap partially a number of spin packets (Fig. 1). This means that electrons in one of these spin packets will have a probability $\tau$ of being in a polarizing region. The value $\tau$ decreases with increasing values of $\Delta = (\omega_d - \omega_{ev})/\gamma_e$ ($\omega_d$ is the resonant frequency of the involved spin packet and $\omega_{ev}$ equals $\omega \pm \omega_n$) and is given by

$$\tau = \delta H \cdot g(\Delta)/\int_{-\infty}^{+\infty} g(\Delta) \, d\Delta = \delta H \cdot g(\Delta). \quad (4)$$

$g(\omega - \omega_n)$ the normalized line from of the spin packet. The average time an electron spends in the polarizing and non polarizing region of the spin packet respectively is then:

$$t_p = T_{2o}/[1 - \delta H \cdot g(\Delta)] \quad \text{and} \quad t_e = T_{2e}/[\delta H \cdot g(\Delta)]. \quad (5)$$

The thermal contact between the paramagnetic centre and the surrounding nuclei is then, for sufficiently strong microwave power, present during $t_p$ and practically absent during $t_e$.

We will now assume that the $N_p$ "polarizing" electrons have a value of $\Delta$ lying between the limits $-\Delta_L$ and $+\Delta_L$. These electrons will for sufficiently strong microwave power contribute continuously to the polarization of the surrounding nuclei, even when they have only a probability $\tau$ of being in the polarizing region.

The bulk nuclei are polarized due to the thermal contact via spin diffusion with the nuclei near the "polarizing" electrons. In order to simplify calculations we will assume that the nuclear polarization is equal to the bulk polarization $P$ for $r > d + a$ or $b + a$ and equal to $P_1$ in a shell with $d < r < d + a$ or $b < r < b + a$. The enhancement of the bulk polarization is mainly brought about via nuclei with distances between $d$ (the diffusion barrier, in the case of rapid spindiffusion) respectively $b$ (the pseudo potential radius in the case of diffusion limited polarization) and $d + a$ respectively $b + a$, where $a$ is the lattice parameter. The influence of nuclei with $r < d$ or $b$ can be neglected for the case of spin diffusion and the direct interaction can be neglected for $r > b + a$ or $d + a$ due to the fact that this interaction decreases rapidly with increasing $r$.

The polarization $P_1$ is assumed to be the same for all shell nuclei and lies somewhere between $P$ and $P_1$ (polarization of the polarizing electron in the rotating frame) depending essentially on $r$ and on the thermal contacts with the polarizing electron and with the nuclear spin system.

The nuclear spin system ($r > b + a$ or $d + a$) is now, on one hand, in thermal contact with $N_p$ shells, with external radii $d + a$ or $b + a$, containing $n_1$ nuclei at a spin temperature $T_1$ corresponding to $P_1$ ($T_1$ varies with $r$) and, on the other hand, with $N_7$ relaxing centres at a spin temperature $T_1$.

When the condition for the solid state effect is fulfilled in the centre of the investigated ESR line then the polarization $P$ of the bulk nuclei is described by the following equation

$$\frac{dP}{dt} = -\frac{N}{n} \sum_{\Delta_1} \frac{G(\Delta)}{T_{1t}} \cdot N \cdot d\Delta - \frac{P - P_g}{T_{1t}}. \quad (6)$$

$G(\Delta)$ is the number of paramagnetic centres with a value $\Delta_1$ with the normalized ESR line shape $G(\Delta)$. We will assume that $G(\Delta) \approx G(0)$ for $-\Delta_L < \Delta < +\Delta_L$. ($N =$ total number of paramagnetic centres per cm$^3$, $a =$ the ratio of the surface of the investigated ESR line to the sum of the surfaces of all lines in the ESR spectrum, $1/T_{1t} =$ flip-flop probability for two neighbouring nuclei, and $T_{1n} =$ spin lattice relaxation time of the nuclear spin system, due to $N_7$ relaxing centres.)
3. Calculation of the Enhanced Nuclear Polarization and the Polarization Time as a Function of the Microwave Power

With Eq. (6) we are able to calculate the enhancement in a stationary state, provided that we know the parameters $P_1$ and $\omega_0$. It is possible to write $P_1$ as a function of $P$ and $\Pi_1$, while $\Pi_1$ is influenced by two mechanisms: a spin lattice relaxation mechanism in the rotating frame which tends to give the electrons a polarization $\Pi_0$ and the thermal contact with shell nuclei which tends to equalize $P_1$ and $\Pi_1$. We are therefore able to express $\Pi_1$ in terms of $\Pi_0$ and $P_1$. We have thus two equations with two unknowns $P_1$ and $\Pi_1$, which can be solved. When we insert the value of $P_1$ obtained in Eq. (6) we are able to calculate $P$.

We can now write out equations for the polarization $P_1$ of the shell nuclei during $t_p$ and $t_\tau$ respectively. During $t_p$ the shell nuclei are in good thermal contact with both the nuclear spin system and the polarizing electron. The thermal contact between the shell nuclei and the rotating frame electron improves proportionally with increasing microwave power and is characterized by $T_{\text{pex}}$ given by Eq. (1 c). [Since the electron is supposed to have only direct interaction with the shell nuclei Eq. (1 c) can be simplified.] We get

$$
\frac{dP_1}{dt}_{\text{pol}} = - \left(\frac{P_1 - \Pi_1}{n_1 T_{\text{pex}}} - \frac{(P_1 - P)}{T_{\text{ft}}}ight) 
= - P_1 \left(\frac{1}{n_1 T_{\text{pex}}} + \frac{1}{T_{\text{ft}}}\right) + \frac{\Pi_1}{n_1 T_{\text{pex}}} + \frac{P_1}{T_{\text{ft}}}.
$$

(7)

During $t_\tau$ the shell nuclei are in good thermal contact with the nuclear spin system, but in bad thermal contact with the paramagnetic centre. When we neglect the relaxation of shell nuclei due to direct interaction with the electron, we can write

$$
(P_1/dt)_{\text{pol}} \approx - \frac{(P_1 - P)}{T_{\text{ft}}}. 
$$

(8)

$P_1$ reaches an equilibrium value when an increase during $t_p$ [Eq. (7)] is compensated by a decrease during $t_\tau$ [Eq. (8)]

$$
t_p \frac{dP_1}{dt}_{\text{pol}} = - t_\tau (dP_1/dt)_{\text{rel}}.
$$

The equilibrium value is given by:

$$
P_1 = \frac{(\Pi_1 \tau/n_1 T_{\text{pex}}) + (P/T_{\text{ft}})}{(\tau/n_1 T_{\text{pex}}) + (1/T_{\text{ft}})}. 
$$

(9)

The polarization of the electron in the rotating frame $\Pi_1$ in Eq. (9) is determined by two factors: 1. A spin lattice relaxation mechanism which tends to restore a rotating frame spin temperature $T_{\text{s0}} \approx \left(\gamma_a/\gamma_e \right) T_{\text{ft}}$; and 2. A thermal contact between the polarizing electron and the shell nuclei which tends to equalize the spin temperatures of both in a characteristic time $T_{\text{pex}}$ and which is present during $t_p$ and absent during $t_\tau$.

During $t_\tau$, $\Pi_1$ is governed by the following relation:

$$
\left(\frac{d\Pi_1}{dt}\right)_{\text{rel}} = - \left(\frac{(P_1 - \Pi_1)}{P_{\text{ex}}} - \frac{(P_1 - \Pi_0)}{T_{\text{e}}}ight)
= - \left(\frac{1}{T_{\text{pex}} + 1/T_{\text{e}}}\right) \frac{P_1}{T_{\text{pex}}} + \frac{\Pi_0}{T_{\text{e}}}. 
$$

(10)

$T_{\text{e}}$ is the electron spin lattice relaxation time in the rotating frame.

During $t_\tau$ the polarizing electron is in poor thermal contact with the shell nuclei. If we assume that during $t_\tau$ a rotating frame spin temperature can also be defined for the electron, then it will go back to its equilibrium spin temperature $T_{\text{s0}}$ in a characteristic time $T_{\text{e}}$

$$
\left(\frac{d\Pi_1}{dt}\right)_{\text{rel}} = - \left(\frac{(P_1 - \Pi_0)}{T_{\text{e}}}\right). 
$$

(11)

With Eqs. (10) and (11) we are thus able to calculate the value of $P_1$ in Eq. (9). In the evaluation of $\Pi_1$ we will distinguish two cases: 1. $t_\tau > T_{\text{e}}$ and 2. $t_\tau < T_{\text{e}}$.

1. $t_\tau > T_{\text{e}}$

Under this condition the polarizing electron has during $t_\tau$ time to reach its equilibrium value $\Pi_0$. During $t_p$, $\Pi_1$ is initially $\Pi_0$ and changes according to Eq. (10). In order to simplify calculations we take for $\Pi_1$ in Eq. (9), the average value during $t_p$,

$$
\langle \Pi_1 \rangle = \Pi_{\text{im}} + \left\langle \Pi_0 - \Pi_{\text{im}} \right\rangle A. 
$$

(12a)

with

$$
\Pi_{\text{im}} = \frac{\Pi_0 T_{\text{e}} + P_1 T_{\text{pex}}}{1/T_{\text{e}} + 1/T_{\text{pex}}} [\text{see Eq. (10)}].
$$

and

$$
A = \frac{1}{1 + \text{exp}\left(-\left(1/T_{\text{e}} + 1/T_{\text{pex}}\right) t_p\right)}. 
$$

(12b)

We are now able to calculate the polarization $P$ of the nuclear spin system in a stationary state from Eqs. (6), (9), (12a) and (12b). The enhancement is then given by:

$$
E = \frac{2 \times N G(0)}{n} \left(\frac{n_1}{T_{\text{ft}} + T_{\text{a}}/\tau}\right) \frac{dA}{dJ} \frac{\Pi_0 + 1}{P_0} \frac{1}{T_{\text{in}}}.
$$

(13)

The characteristic time $T_p$ in which the nuclear system reaches its equilibrium polarization is, according to Eqs. (6), (9), (12a) and (12b), given by

$$
\frac{1}{T_p} = \frac{2 \times N G(0)}{n} \left(\frac{n_1}{T_{\text{ft}} + T_{\text{a}}/\tau}\right) \frac{dA}{dJ} \frac{1}{T_{\text{in}}}. 
$$

(14)
\[ T_a \text{ in both equations is given by:} \]
\[ \frac{1}{T_a} = \frac{T_{\text{pe}} + T_{1e} A}{n_1 T_{\text{pe}} (T_{\text{pe}} + T_{1e})}. \quad (15) \]

For sufficiently low microwave power \( T_a \) equals \( n_1 T_{\text{pe}} \), while for high microwave power \( T_a \) reaches a minimum value \( T_{\text{pe}} n_1 / (1 + T_{1e}/t_p) \). When the maximum enhancement in the last case is smaller than \( \gamma_n/T_n \) the polarizing electrons in the rotating frame are heated up.

In the equations for \( E \) and \( T_F \), \( \Delta_L \) is still unknown. \( 2 \Delta_L \) is the width of the region in the ESR line where “polarizing” electrons have their Larmor frequencies. We define here a “polarizing” electron somewhat loosely as an electron which gives its shell nuclei a continuous polarization \( P_1 \) higher than \( P \). During \( t_p \), \( P_1 \) is for sufficient microwave power larger than \( P \) while we assume that this condition during \( t_p \), where \( P_1 \) tends to \( P \) according to Eq. (8), is fulfilled for \( T_{1f} > t_F \). An electron is therefore in a “polarizing” state when its value \( t_p \) is smaller than \( T_{1f} \).

\( \Delta_L \) is now the value \( \Delta \) of electrons for which \( T_{1f} \) equals \( t_p \), and can be calculated with \( T_{1f} = t_p \), Eq. (5) and the known shape of the spin packet.

2. \( t_p < T_{1e} \)

Here \( \Pi_1 \), during \( t_p \) does not have the time to go back to \( \Pi_0 \). \( \Pi_1 \) can be obtained from Eq. (10) and (11) by the condition

\[ t_p (d\Pi_1/dt)_{\text{pol}} = -t_r (d\Pi_1/dt)_{\text{rel}} \]

and we get:

\[ \Pi_1 = \frac{T_{1e}}{2 \Delta L} \int_0^{\Delta_L} \frac{d\Pi_0}{T_{1e} + T_{\text{pe}}/t + T_{1f}/n_1} + \frac{1}{P_0} \frac{1}{T_{1n}}. \quad (16) \]

The polarization \( P \) of the nuclear spin system can in a stationary state, be expressed with the help of Eqs. (6), (16), and (9). The enhancement becomes

\[ E = \frac{P}{P_0} = \frac{2 \Delta L}{n} \int_0^{\Delta_L} \frac{d\Pi_0}{T_{1e} + T_{\text{pe}}/t + T_{1f}/n_1} + \frac{1}{P_0} \frac{1}{T_{1n}}. \quad (17) \]

The polarization rate of the nuclear spin system is:

\[ \frac{1}{T_p} = \frac{2 \Delta L}{n} \int_0^{\Delta_L} \frac{d\Pi_0}{T_{1e} + T_{\text{pe}}/t + T_{1f}/n_1} + \frac{1}{P_0} \frac{1}{T_{1n}}. \quad (18) \]

The maximum value of \( E \) is reached for high microwave power such that \( T_{\text{pe}}/t \) is much smaller than \( T_{1e} + T_{1f}/n_1 \). The polarizing electrons then receive during \( t_p \) more energy from the nuclear spin system than they can dissipate into the lattice during \( t_p + t_r \). The electrons in the rotating frame are consequently heated up and \( \Pi_1 \) reaches a minimum value which can be calculated from Eqs. (9) and (16). \( \Delta_L \) can be calculated in the same way as for case one.

4. Local Field Fluctuations Induced by Surrounding Nuclei

So far we have neglected the influence of field fluctuations induced by surrounding nuclei. These fluctuations, however, influence \( P_{1e} \) and therefore the enhancement of the bulk nuclei. Due to these field fluctuations, the paramagnetic centre spends an average time \( t_p \) and \( t_R \) in the “polarizing” (2 \( \Delta_L \)) and “nonpolarizing” region of the ESR line respectively. The polarization \( P_1 \) is therefore modulated by these field fluctuations.

During \( t_p \), \( P_1 \) tends to an equilibrium value \( P_{1e} \) which lies somewhere between \( \Pi_0 \) and \( P \) depending on \( T_{1f} \) and on \( T_b \) [\( T_b \) is \( T_a/t \) in the first case (Eqs. (9) and (12)) and \( n_1 (T_{1e} + T_{\text{pe}}/t) \) in the second case (Eqs. (9) and (16))]. The enhancement becomes

\[ E = \frac{P_{1e}}{P_0} = \frac{\Pi_0}{T_b + 1/T_{1f}}. \quad (19) \]

The shell nuclei will reach this equilibrium polarization in a characteristic time \( 1/T_b + 1/T_{1f} \). During \( t_R \), \( P_1 \) tends to \( P \) according to Eq. (8).

We will discuss the influence of the field fluctuations induced by surrounding nuclei, for one particular case, where \( t_p \) is much shorter than \( 1/(1/T_b + 1/T_{1f}) \) and where \( T_R \) is large compared with \( T_{1f} \). The polarization is then always nearly equal to \( P \) and the field fluctuations have the same effect as if \( T_{1f} \) in Eq. (19) were much shorter than \( T_b \). The limitation of the Zeeman energy transport between the polarizing electron and the nuclear spin system caused by spin diffusion (\( T_{1f} \)), therefore disappears when field fluctuations induced by surrounding nuclei are such that the conditions \( t_p < 1/(1/T_b + 1/T_{1f}) \) and \( t_R > T_{1f} \) are fulfilled. In this case \( T_{1f} \) in the Eqs. (13), (14), (17), and (18) can be omitted.
5. Apparatus and Experimental Results

The ESR measurements were done with an AEG X-band spectrometer with a microwave frequency of 9.3 GHz.

The strong microwave field needed during dynamic polarization experiments, for the saturation of the electron spins was delivered by a 6 Watt two cavity Klystron (Varian 50B) with a fixed frequency of 9.5 GHz. A cylindrical cavity was used which could be tuned easily to the fixed klystron frequency. The microwave power incident on the coupling hole could be regulated with a 50 db attenuator.

For field modulation experiments a rectangular AEG X-band cavity was used (TE 102 mode) where the skin effect was negligible up to 150,000 Hz.

Both the polarization and spin lattice relaxation time of the nuclear spin system and the enhancement were measured with a pulse spectrometer, the frequency of which could be varied over a range of 14-15 MHz. The NMR signal was detected with a coil of 7 turns around the crystal which, when inserted into the cavity, did not influence its Q. For one case a 48 MHz pulse spectrometer was used.

For measurements at 80 °K the CaF₂ single crystal was placed in vacuum and glued to a copper rod in thermal contact with liquid nitrogen. For measurements at 290 °K the crystal was cooled with a stream of nitrogen gas the temperature of which could be regulated.

The experiments were performed with single crystals of CaF₂ (Quartz et Silice) containing H atoms as paramagnetic impurities. The paramagnetic resonance of these centres has been investigated by HALL and SCHUMACHER. The H atoms were introduced into the crystal, according to their recipe, by heating CaF₂ single crystals in a H₂-atmosphere (10 cm Hg) at 900 °K for several days and by irradiating them afterwards with X-rays for ten hours at 190 °K. H atoms in CaF₂ are stable up to 420 °K. The maximum concentration obtained was 1.7·10¹⁸ cm⁻³. The concentration was determined by comparing the signal from the H atoms with that from lignite containing a known number of paramagnetic centres per gram.

All our experiments were performed with a H atom concentration of 1.7·10¹⁸ cm⁻³ and with H₀ parallel to the [110] direction of the single crystal. The ESR spectrum consisted then of two groups of thirteen well separated inhomogeneously broadened lines with a line width $\Delta H_e = 2.50$ Oe ($\Delta H = 2\pi \gamma H_e T_1e T_2o$) of one of these lines was equal to unity for a microwave power of 0.5 mW. The spin lattice relaxation time $T_1e$ as a function of the temperature has been measured, for H atoms, by FELDMAN et al. ⁹

* Dynamic polarization in hydrogen doped single crystals of CaF₂ was also measured by BURKERSRODE ¹⁰ (who, due to insufficient microwave power only obtained an enhancement of 45) and SOOK LEE et al. ¹¹ (who did not attempt to justify the strong solid state effect obtained).

¹¹ SOOK LEE, V. P. JACOBSEN, and TH. V. HYNEs, Phys. Rev. Letters 17, 1245 [1966].
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Fig. 3. The Enhancement $E$ of the fluorine polarization measured as a function of microwave power at 290 °K in single crystals of CaF₂ with H atoms (circles), compared with the theoretical $E - H_f^2$ curve (solid line).

Fig. 4. The enhancement of the fluorine polarization measured as a function of microwave power at 80 °K in single crystals of CaF₂ containing H atoms.

**Polarization time $T_P$**

The characteristic polarizing time $T_P$ in which the nuclear spin system reaches its solid state effect enhanced equilibrium polarization, was measured as a function of microwave power at 290 °K and 80 °K. The time dependence of the polarization was in all cases exponential. The values of $T_P$ are given in Table 2.

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<th>Microwave Attenuation (db)</th>
<th>$T_P$ (s)</th>
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<td>9 s</td>
</tr>
<tr>
<td>80 °K</td>
<td>9 s</td>
</tr>
</tbody>
</table>

Table 2.

**Modulation effect**

The static magnetic field $H_0$ was modulated and the influence of this field modulation on the nuclear enhancement was studied. In CaF₂ at 290 °K the ratio $E_{mod}/E$ (ratio of the enhancement with and without field modulation) was measured as a function of the modulation frequency $\nu_m$ and modulation amplitude $H_m$. The results are given in Fig. 5.

6. Discussion of the Experimental Results

**Nuclear relaxation**

In CaF₂ at 290 °K nuclear relaxation occurs mainly via rapid spin diffusion. This can be concluded from the fact that the measured values of $T_{1n}$ are proportional to $H_0^{1.5}$. According to BLUMBERG the nuclear spin system is relaxed via rapid spin diffusion when $T_{1n}$ is proportional to $H_0^2$, while in the case of diffusion limited relaxation $T_{1n}$ is proportional to $H_0^{1/2}$ provided $T_{1e}$ is independent of $H_0$.

From nuclear relaxation time measurements it is also concluded that at 290 °K nuclear relaxation is caused by H atoms and at 80 °K by other centres which are introduced into the crystal by X-irradiation, along with the H atoms (see Table 1). The supposition that nuclear relaxation at 80 °K is more effectively executed via other paramagnetic centres is supported by the fact that the ratio of $T_{1n}$ at 80 °K and 290 °K is much smaller than one would theoretically expect [Eq. (1 b)]. Since $T_{1n}$ is in our case proportional to $T_{1e}$ both at 80 °K and at 290 °K ($T_{1e}$ is resp. $3 \times 10^{-3}$ s and $3 \times 10^{-6}$ s) one would expect this ratio to be 1000 whereas the experimental value is only 4.5.

$E$ at 290 °K

At room temperature Eqs. (13) and (14) must be applied since $T_{1e}(3 \times 10^{-6}$ s) is shorter than $t$, which is given by Eq. (5). ($T_{2e} = 1.2 \times 10^{-7}$ s, $\delta H = 0.018$ Oe, $\xi = 0.5$ Oe values which will be justified later.) $T_{1e}$ in these equations can be omitted since the field fluctuations induced by neighbouring nuclei are very rapid.

Neglecting also the second term in the nominator of Eq. (13) we get:

\[
E = \frac{[aNG(0)/nT_a]_s}{[aNG(0)/nT_a]_s + \frac{\Delta L}{\Delta L}}. 
\]

(20)

For \( \Delta L > \xi \) the main contribution to the integral in Eq. (20) comes from electrons with \(-\frac{1}{2}\xi < \xi < \frac{1}{2}\xi\) where \(g(\Delta)\) has its largest value. The effective width of the polarizing region is thus approximately the spin packet width \(\xi\).

Assuming \(G(0) \cdot \Delta H_e \approx 1\) Eq. (20) becomes

\[
E = \frac{(a \Delta H n_n/n_T \Delta H_e \cdot (\Pi_s) \cdot T_{1n}}{(a \Delta H n_n/n_T \Delta H_e) \cdot T_{1n} + 1}. 
\]

(21)

The theoretical \(E - H_z^2\) curve given by Eq. (21) coincides with the experimental curve when \(\Delta H = 0.018\) Oe, \(t_0 \approx T_{2o} = 1.2 \cdot 10^{-7}\) s and when \(T_{\text{pex}}\) equals \(6 \cdot 10^{-8}\) s for one Watt microwave power.

\(T_o\) and \(T_{\text{pex}}\) enter in Eq. (21) via \(T_a\), Eq. (15).] The value of \(\Delta H\) obtained in this way (0.018 Oe) is in good agreement with \(\Delta H\) calculated from Eq. (2). This equation gives \(\Delta H = 0.02\) Oe for \(d = 15\) Å and \(\Delta H = 2.5\) Oe.

The value \(t_0 \approx T_{2o} = 1.2 \cdot 10^{-7}\) s corresponds to a spin packet width \(\xi\) of 0.5 Oe. When we calculate the spin packet width with the help of the H atom concentration \(1.7 \cdot 10^{18}\) cm\(^{-3}\) on the assumption that paramagnetic centres are arranged regularly, we obtain \(\xi = 0.1\) Oe. The fact, however, that the unpaired electrons are randomly distributed makes the average value of \(\xi\) considerably larger and the value of 0.5 Oe is therefore not unreasonable.

\(T_{\text{pex}}\) for one watt calculated with the \(E - H_z^2\) curve agrees reasonably well with the value calculated from the experimental values of \(s\) for one watt and \(T_{1n}\) at 290 °K using the expression \(T_{\text{pex}} = (N/n) \cdot T_{1n} / (s+1)\) [Eqs. (1b) and (1c)]. In this way one obtains \(3.4 \cdot 10^{-8}\) s \((T_{1n} = 2\) sec, \(s = 2000\) for 1 watt).

\(T_{1n}\) at 290 °K

It is possible to calculate \(T_{1n}\) at 290 °K with the experimental values of \(E\) (Fig. 3) and \(T_{1n}\) using Eqs. (13) and (14). Values of \(T_{1n}/T_{1p}\) obtained in this way are plotted against the attenuation of the microwave power. They agree very well with the measured values of \(T_{1n}/T_{1p}\) (Fig. 6).

At 80 °K Eqs (17) and (18) must be applied since \(T_{1e} (3 \cdot 10^{-3}\) s\) is larger than \(t_e = T_{2e}/\tau\) for all “polarizing” electrons (with \(-\Delta L < \xi < +\Delta L\)). We defined a “polarizing” centre as a paramagnetic centre which fulfils the condition \(T_{1e} > t_e\) and which has therefore in our case a value of \(\xi\) larger than the ESR line width. All electrons in the investigated ESR line are therefore in a “polarizing” state and we write \(\Delta H_e\) instead of \(2\Delta L\).

Paramagnetic centres have in our case a value of \(\Delta L\) when \(\tau\) equals \(0.2 \cdot 10^{-3}\). Assuming that spin packets have a Gaussian shape, \(\tau = \Delta H \cdot g(\Delta)\) is equal to \(0.2 \cdot 10^{-3}\) for spin packets with \(\Delta L = \pm 3\xi\) \((\Delta H = 0.018\) Oe and the spin packet width \(\xi\) is 0.5 Oe). The width of the “polarizing” region at 80 °K is then equal to \(2\Delta L = 6\xi = 3\) Oe and is larger than the ESR line width. All electrons in the investigated ESR line are therefore in a “polarizing” state and we write \(\Delta H_e\) instead of \(2\Delta L\).

We then obtain \(E_{\text{max}} = 7.5\) using the following values \(\alpha = 1/11, N = 1.7 \cdot 10^{18}\) cm\(^{-3}\), \(\Pi_s/P_0 = 700, T_{1n} = 9\) s, \(n = 5 \cdot 10^{22}\) k/cm\(^3\) and \(T_{1e} = 3 \cdot 10^{-3}\) s. This value of \(E_{\text{max}}\) agrees reasonably well with the measured value of four.
The low enhancement at 80 °K is attributed to the fact that nuclear relaxation at this temperature is mainly determined by unknown paramagnetic centres and that the polarizing electrons in the rotating frame are heated up. If the unknown centres were not present $T_{1n}$ should be 2000 s and $E_{\text{max}}$ should be much higher.

Modulation effect

The importance of the modulation effect was already studied in a previous paper\textsuperscript{1}. The effect could be explained, but much too large a value of $\delta H$ had to be chosen in order to fit the experimental curve.

We will now investigate whether, at 290 °K, the experimental $E_{\text{mod}}/E - v_m$ curve can be matched to the theoretical curve taking into account the assumptions of this work. This was done for a modulation amplitude of 2.8 Oe, at a microwave power of one watt where $E$ equals 150. The theoretical curve can be calculated with Eqs. (21) and Eq. (8) of ref. 1. We get, neglecting the second term in the denominators of the last equation

$$\frac{E_{\text{mod}}}{E} = \frac{(1/T_{a}'/T')}{(\delta H/\Delta H_0) \cdot (1/T_{a})} \cdot \frac{(z n \Delta H n_i/n T_{a} \Delta H_0) \cdot T_{1n} + 1}{(z n_i/n T_a'/T') \cdot T_{1n} + 1}.$$  

(23)

$T_a'$ and $T'$ are here the values of $T_a$ [Eq. (15)] and $T = t_p/t_r$ where $t_p$ and $t_r$ are replaced by

$$t_p' = \frac{2 \delta H}{\pi 2 \Delta H_m} \cdot \frac{1}{2 \tau_m}$$

and $t_r' = \frac{1}{2 \tau_m}$ for $\delta H \ll \Delta H_m$.

The second ratio on the right side in this equation is approximately equal to one. $T_a$ for one watt is roughly 200/150 times the minimum value of $T_a$ [$T_{a, \text{min}} = T_{1e} n_i/(1 + T_{1e}/t_p) = 1.2 \cdot 10^{-7} \cdot n_i$ sec]. We get:

$$\frac{E_{\text{mod}}}{E} = \frac{1.6 \cdot 10^{-7} T_{1e} A'}{(T_{1e} + \Delta H_0) \cdot T_{\text{pex}}}.$$  

(24)

The theoretical $E_{\text{mod}}/E - v_m$ curve [Eq. (24)] matches the experimental points very well, if we choose the parameters $\delta H$ and $T_{\text{pex}}$ at one watt to be 0.013 Oe and 3.3 $\cdot 10^{-8}$ sec respectively. This is in good agreement with the values of $\delta H$ and $T_{\text{pex}}$ calculated from the experimental $E - H_1^2$ curve (0.018 Oe and 6 $\cdot 10^{-8}$ sec respectively) and with $\delta H$ calculated from Eq. (2).

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