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 fulfil $\omega_e = \omega + \omega_n$ 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 flipping 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[1] 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[2], was supposed to be in thermal contact with two types of paramagnetic centres: a few polarizing centres N_p, which fulfil 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[3], 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 γ_e/γ_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 γ_e/γ_n.

The following formula for the enhancement was obtained:

$$E = \frac{P}{P_0} = \frac{[N_p/n] \cdot [1/(T_{1e}+T_{exp})] \cdot [\Pi_0/P_0] + 1/T_{1n}}{[N_p/n] \cdot [1/(T_{1e}+T_{pex})] + 1/T_{1n}} . \tag{1 a}$$

In Eq. (1 a)

$$1/T_{1n} = N_r \int_d^\infty [C/r^6]\ 2\pi r^2\, dr = \tfrac{4}{3}\pi N_r \cdot C/d^3 \tag{1 b}$$

for rapid spin diffusion[4] is the bulk nuclear relaxation rate due to the N_r relaxing paramagnetic centres;

$$1/T_{pex} = n \int_d^\infty [(s+1)\, C/r^6]\ 4\pi r^2\, dr = \tfrac{4}{3}\pi n \cdot (s+1)\, C/d^3 \tag{1 c}$$

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 $r > d$; $s = \gamma_e^2 H_1^2 T_{1e} T_{2e}$; N_p = number of polarizing electrons per/cm^3; n = number of fluorine nuclei per cm^3; T_{1e} = electron spin-lattice relaxation

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time; $C \approx \frac{2}{5}\, \gamma_e^2 \gamma_n^2 \hbar^2 S(S+1) \cdot T_{1e}/(1+\omega_n^2 T_{1e}^2)$. Π_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 δH of the polarizing region in the ESR line, related to N_p [1], calculated with Eq. (1 a) and the experimental value of $E_{max} = 190$ ($\delta H = 0.4$ Oe) is much higher than one would expect theoretically ($\delta H = 0.02$ Oe).

2. A second difficulty arizes from the fact that the theoretical $E - H_1^2$ 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 [6] 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 modulation effect, the microwave power depence of the enhancement and of the polarization time, can be described in a satisfactory way. This will be shown in the following.

1. Width δH 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 δH. Knowledge of δH 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 δH.

The nuclear Larmor frequencies ω_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. ω_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) [2] or d (for rapid spin diffusion [4]), 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 μ_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 $\omega_e/\gamma_e = \omega/\gamma_e \pm \omega_n/\gamma_e$ 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

$$\delta H \approx (\gamma_n/\gamma_e)\,(\Delta H + 2 \cdot \mu_e/r^3) \qquad (2)$$

with $r = d$ or b when $b > d$.

With Eq. (2), for a CaF_2 single crystal containing H-atoms with $[110] \parallel \overline{H}_0$, the aforementioned value of 0.02 Oe (with $d = 15$ Å [7] and $\Delta H = 2.5$ 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 (δH). 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_p' 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 ξ (we assume that spectral diffusion and cross

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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 δH is smaller than ξ, 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 τ of being in a polarizing region. The value τ decreases with increasing values of $\Delta = (\omega_\Delta - \omega_{ev})/\gamma_e$ (ω_Δ is the resonant frequency of the involved spin packet and ω_{ev} equals $\omega \pm \omega_n$) and is given by

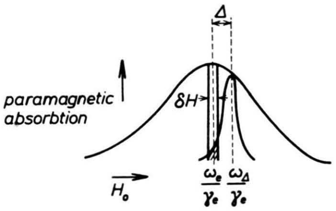

Fig. 1. Inhomogeneous ESR line where the polarizing region is partially overlapping a spin packet.

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

$g(\omega - \omega_0)$ 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:

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

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_r.

We will now assume that the $N_p{}'$ "polarizing" electrons have a value of Δ 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 τ 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 repidly with increasing r. The polarization P_1 is assumed to be the same for all shell nuclei and lies somewhere between P and Π_1 (polarization of the polarizing electron in the rotating frame) depending essentially on τ 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 τ) and, on the other hand, with N_r relaxing centres at a spin temperature T_L.

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

$$\frac{dP}{dt} = -\frac{\alpha}{n} \int_{-\Delta_L}^{+\Delta_L} \frac{n_1 (P - P_1)}{T_{ff}} \cdot G(\Delta) \cdot N \cdot d\Delta - \frac{P - P_0}{T_{1n}}. \qquad (6)$$

$G(\Delta)\, N\, d\Delta$ is the number of paramagnetic centres with a value Δ, 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, α = the ratio of the surface of the investigated ESR line to the sum of the surfaces of all lines in the ESR spectrum, $1/T_{ff}$ = flip-flop probability for two neighbouring nuclei, and T_{1n} = spin lattice relaxation time of the nuclear spin system, due to N_r 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 Δ_L. It is possible to write P_1 as a function of P and Π_1, while Π_1 is influenced by two mechanisms: a spin lattice relaxation mechanism in the rotating frame which tends to give the electrons a polarization Π_0 and the thermal contact with shell nuclei which tends to equalize P_1 and Π_1. We are therefore able to express Π_1 in terms of Π_0 and $P1$. We have thus two equations with two unknowns P_1 and Π_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_r 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_{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

$$\left(\frac{dP_1}{dt}\right)_{pol} = -(P_1 - \Pi_1)/n_1 T_{pex} - (P_1 - P)/T_{ff} \qquad (7)$$
$$= -P_1(1/n_1 T_{pex} + 1/T_{ff}) + \Pi_1/n_1 T_{pex} + P/T_{ff}.$$

During t_r 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

$$(dP_1/dt)_{rel} \approx -(P_1 - P)/T_{ff}. \qquad (8)$$

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

$$t_p(dP_1/dt)_{pol} = -t_r(dP_1/dt)_{rel}.$$

The equilibrium value is given by:

$$P_1 = \frac{(\Pi_1 \tau/n_1 T_{pex}) + (P/T_{ff})}{(\tau/n_1 T_{pex}) + (1/T_{ff})}. \qquad (9)$$

The polarization of the electron in the rotating frame Π_1 in Eq. (9) is determined by two factors: 1. A spin lattice relaxation mechanism which tries to restore a rotating frame spin temperature $T_{S0} \approx (\gamma_n/\gamma_e) T_L$; 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_{pex} and which is present during t_p and absent during t_r.

During t_p, Π_1 is governed by the following relation:

$$\left(\frac{d\Pi_1}{dt}\right)_{pol} = -(\Pi_1 - P_1)/T_{pex} - (\Pi_1 - \Pi_0)/T_{1e}$$
$$= -(1/T_{pex} + 1/T_{1e})\,\Pi_1 + P_1/T_{pex} + \Pi_0/T_{1e}. \qquad (10)$$

T_{1e} is the electron spin lattice relaxation time in the rotating frame.

During t_r the polarizing electron is in poor thermal contact with the shell nuclei. If we assume that during t_r a rotating frame spin temperature can also be defined for the electron, then it will go back to its equilibrium spin temperature T_{S0} in a characteristic time T_{1e}

$$(d\Pi_1/dt)_{rel} = -(\Pi_1 - \Pi_0)/T_{1e}. \qquad (11)$$

With Eqs. (10) and (11) we are thus able to calculate the value of Π_1 in Eq. (9). In the evaluation of Π_1 we will distinguish two cases: 1. $t_r > T_{1e}$ and 2. $t_r < T_{1e}$.

1. $t_r > T_{1e}$

Under this condition the polarizing electron has during t_r time to reach its equilibrium value Π_0. During t_p, Π_1 is initially Π_0 and changes according to Eq. (10). In order to simplify calculations we take for Π_1 in Eq. (9), the average value during t_p,

$$\langle \Pi_1 \rangle = \Pi_{1m} + (\Pi_0 - \Pi_{1m})\,A. \qquad (12a)$$

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

and $$A = \frac{1 - \exp\{-(1/T_{1e} + 1/T_{pex})\,t_p\}}{(1/T_{1e} + 1/T_{pex})\,t_p}. \qquad (12b)$$

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

$$E = \frac{P}{P_0} = \frac{\dfrac{2\alpha N G(0)}{n} \displaystyle\int_0^{\Delta_L} \frac{n_1}{T_{ff} + T_a/\tau}\, d\Delta \cdot \frac{\Pi_0}{P_0} + \frac{1}{T_{1n}}}{\dfrac{2\alpha N G(0)}{n} \displaystyle\int_0^{\Delta_L} \frac{n_1}{T_{ff} + T_a/\tau}\, d\Delta + \frac{1}{T_{1n}}}. \qquad (13)$$

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

$$\frac{1}{T_P} = \frac{2\alpha N G(0)}{n} \int_0^{\Delta_L} \frac{n_1}{T_{ff} + T_a/\tau}\, d\Delta + \frac{1}{T_{1n}}. \qquad (14)$$

T_a in both equations is given by:

$$\frac{1}{T_a} = \frac{T_{\text{pex}} + T_{1e}\,A}{n_1\,T_{\text{pex}}\,(T_{\text{pex}} + T_{1e})}\,. \tag{15}$$

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

In the equations for E and T_P, Δ_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_r, where P_1 tends to P according to Eq. (8), is fulfilled for $T_{ff} > t_r$. An electron is therefore in a "polarizing" state when its value t_r is smaller than T_{ff}.

Δ_L is now the value Δ of electrons for which T_{ff} equals t_r, and can be calculated with $T_{ff} = t_r$, Eq. (5) and the known shape of the spin packet.

2. $t_r < T_{1e}$

Here Π_1, during t_r does not have the time to go back to Π_0. Π_1 can be obtained from Eq. (10) and (11) by the condition

$$t_p\,(\mathrm{d}\Pi_1/\mathrm{d}t)_{\text{pol}} = -\,t_r\,(\mathrm{d}\Pi_1/\mathrm{d}t)_{\text{rel}}$$

and we get:

$$\Pi_1 = \frac{P_1\,\tau/T_{\text{pex}} + \Pi_0/T_{1e}}{\tau/T_{\text{pex}} + 1/T_{1e}}\,. \tag{16}$$

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

$$E = \frac{P}{P_0} = \frac{\dfrac{2\,\alpha\,N\,G(0)}{n}\displaystyle\int_0^{\Delta_L}\frac{\mathrm{d}\Delta}{T_{1e} + T_{\text{pex}}/\tau + T_{ff}/n_1}\cdot\frac{\Pi_0}{P_0} + \frac{1}{T_{1n}}}{\dfrac{2\,\alpha\,N\,G(0)}{n}\displaystyle\int_0^{\Delta_L}\frac{\mathrm{d}\Delta}{T_{1e} + T_{\text{pex}}/\tau + T_{ff}/n_1} + \frac{1}{T_{1n}}}\,. \tag{17}$$

The polarization rate of the nuclear spin system is:

$$\frac{1}{T_P} = \frac{2\,\alpha\,N\,G(0)}{n}\int_0^{\Delta_L}\frac{\mathrm{d}\Delta}{T_{1e} + T_{\text{pex}}/\tau + T_{ff}/n_1} + \frac{1}{T_{1n}}\,. \tag{18}$$

The maximum value of E is reached for high microwave power such that T_{pex}/τ is much smaller than $T_{1e} + T_{ff}/n_1$. 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 Π_1 reaches a minimum value which can be calculated from Eqs. (9) and (16). Δ_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_1 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 Π_0 and P depending on T_{ff} and on T_b [T_b is T_a/τ in the first case (Eqs. (9) and (12)) and $n_1(T_{1e} + T_{\text{pex}}/\tau)$ in the second case (Eqs. (9) and (16))] and which is given by:

$$P_{1e} = \frac{\Pi_0/T_b + P/T_{ff}}{1/T_b + 1/T_{ff}}\,. \tag{19}$$

The shell nuclei will reach this equilibrium polarization in a characteristic time $1/T_b + 1/T_{ff}$. 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 $1/(1/T_b + 1/T_{ff})$ and where T_R is large compared with T_{ff}. The polarization is then always nearly equal to P and the field fluctuations have the same effect as if T_{ff} 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_{ff}), therefore disappears when field fluctuations induced by surrounding nuclei are such that the conditions $t_p < 1/(1/T_b + 1/T_{ff})$ and $t_R > t_{ff}$ are fulfilled[6]. In this case T_{ff} 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 508) 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 CaF_2 single crystal was placed in vacuum and glued to a copper rod in thermal contact with liquid nitrogen [6]. 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 CaF_2 (Quartz et Silice) containing H atoms as paramagnetic impurities. The paramagnetic resonance of these centres has been investigated by HALL and SCHUMACHER [8]. The H atoms were introduced into the crystal, according to their recipe, by heating CaF_2 single crystals in a H_2-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 CaF_2 are stable up to 420 °K. The maximum concentration obtained was $1.7 \cdot 10^{18}\,cm^{-3}$. 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 $1.7 \cdot 10^{18}\,cm^{-3}$ and with H_0 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 (Fig. 2). At room temperature the saturation parameter $s = \gamma_e^2 H_1^2 T_{1e} T_{2e}$ 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].

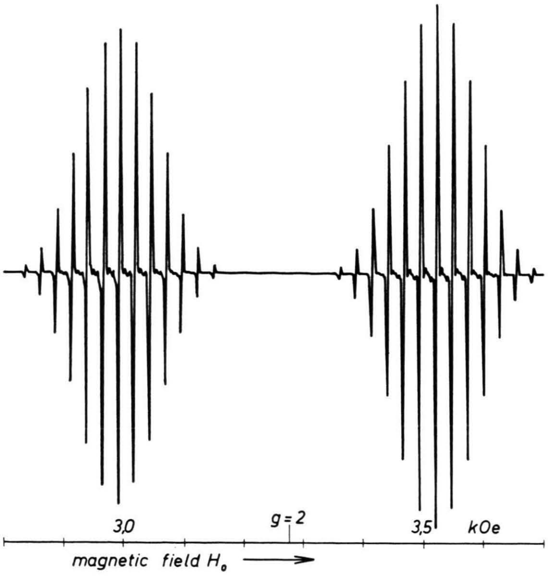

Fig. 2. ESR spectrum of H atoms in CaF_2 with [110] $\parallel$ H_0.

Fluorine spin lattice relaxation time (T_{1n})

T_{1n} was measured as a function of the static magnetic field at 290 °K and we obtained 2 sec and 12 sec respectively for 3.8 kOe and 12 kOe. In order to understand the nuclear relaxation mechanism T_{1n} was measured at 290 °K and 80 °K in a static magnetic field of 3.8 kOe in CaF_2 single crystals with a H atom concentration of $1.7 \cdot 10^{18}\,c/cm^3$ (T_{1n}), in CaF_2 single crystals which were X-irradiated but not heated in a H_2 atmosphere (T'_{1n}), and in CaF_2 single crystals as received from the producer (T''_{1n}). The results are presented in Table 1. The nuclear relaxation was in all cases exponential. The fluorine NMR line width was 2.5 Oe ($T_{2n} = 2 \cdot 10^{-5}$ s).

	T_{1n}	T'_{1n}	T''_{1n}
290 °K	2 s	21 s	30 s
80 °K	9	9	23

Table 1.

Enhancement *

The enhancement was measured as a function of microwave power at 290 °K and 80 °K (Figs. 3 and 4). The condition $\omega_e = \omega + \omega_n$ was fulfilled in the centre of the central line of the high field group. The ratio α of the surface of the investigated line to the total surface of all the lines in the ESR spectrum is 1/11.

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[9] D. W. FELDMAN, J. G. CASTLE JR., and J. MURPHY, Phys. Rev. **138**, A 1208 [1965].

* Dynamic polarization in hydrogen doped single crystals of CaF_2 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).

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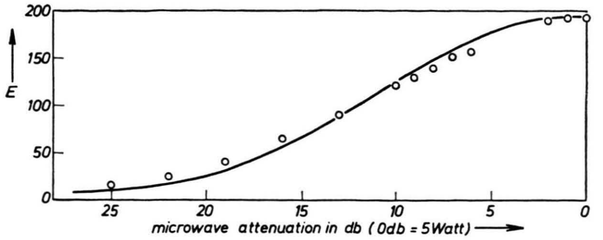

Fig. 3. The Enhancement E of the fluorine polarization measured as a function of microwave power at 290 °K in single crystals of CaF$_2$ with H atoms (circles), compared with the theoretical $E-H_1^2$ curve (solid line).

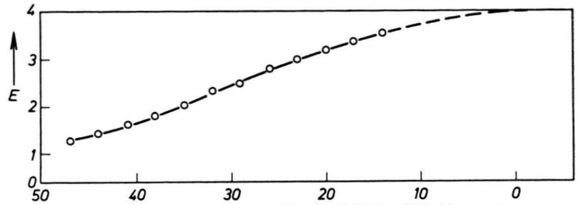

Fig. 4. The enhancement of the fluorine polarizaton measured as a function of microwave power at 80 °K in single crystals of CaF$_2$ containing H atoms.

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.

	0 db	5 db	10 db	15 db	20 db	25 db
290 °K	1.4 s	1.45 s	1.65 s	1.8 s	1.93 s	1.95 s
80 °K		9 s	9 s	9 s	9 s	9 s

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 CaF$_2$ 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 ν_m and modulation amplitude H_m. The results are given in Fig. 5.

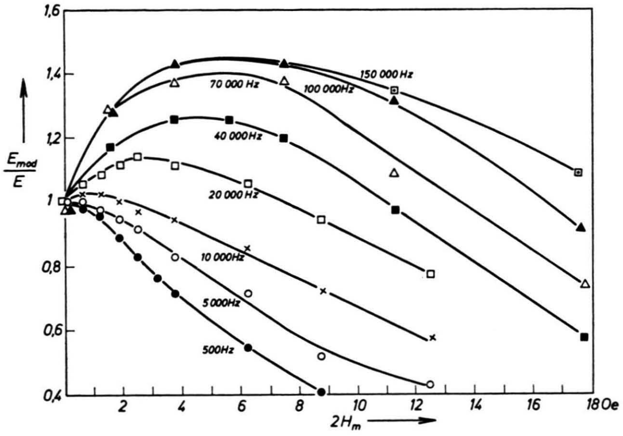

Fig. 5. The experimental values of E_{mod}/E as a function of modulation amplitude H_m and modulation frequency ν_m at 290 °K in CaF$_2$ containing H atoms, with a microwave power such that the enhancement E without modulation equals 150.

6. Discussion of the Experimental Results

Nuclear relaxation

In CaF$_2$ 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 [12] 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. $3\cdot10^{-3}$ s and $3\cdot10^{-6}$ 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 $T_{1e}(3\cdot10^{-6}\text{ s})$ is shorter than t_r which is given by Eq. (5). ($T_{2e}=1.2\cdot10^{-7}$ s, $\delta H=0.018$ Oe, $\xi=0.5$ Oe values which will be justified later.) T_{ff} in these equations can be omitted since the field fluctuations induced by neighbouring nuclei are very rapid.

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

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

$$E = \frac{[\alpha\, N\, G(0)/n\, T_{\mathrm{a}}] \int_{-\Delta_{\mathrm{L}}}^{+\Delta_{\mathrm{L}}} n_1 \cdot \delta H \cdot g(\Delta) \cdot \mathrm{d}\Delta \cdot (\Pi_0/P_0) \cdot T_{1\mathrm{n}}}{[\alpha\, N\, \mathrm{G}(0)/n\, T_{\mathrm{a}}] \int_{-\Delta_{\mathrm{L}}}^{+\Delta_{\mathrm{L}}} n_1 \cdot \delta H \cdot g(\Delta) \cdot \mathrm{d}\Delta \cdot T_{1\mathrm{n}} + 1}. \tag{20}$$

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

Assuming $G(0) \cdot \Delta H_{\mathrm{e}} \approx 1$ Eq. (20) becomes

$$E = \frac{(\alpha\, N\, \delta H\, n_1/n\, T_{\mathrm{a}}\, \Delta H_{\mathrm{e}}) \cdot (\Pi_0/P_0)\, T_{1\mathrm{n}}}{(\alpha\, N\, \delta H\, n_1/n\, T_{\mathrm{a}}\, \Delta H_{\mathrm{e}}) \cdot T_{1\mathrm{n}} + 1}. \tag{21}$$

The theoretical $E - H_1^2$ curve given by Eq. (21) coincides with the experimental curve when $\delta H = 0.018$ Oe, $t_{\mathrm{p}} \approx T_{2\mathrm{e}} = 1.2 \cdot 10^{-7}$ s and when T_{pex} equals $6 \cdot 10^{-8}$ s for one Watt microwave power. [t_{p} and T_{pex} enter in Eq. (21) via T_{a}, Eq. (15).]

The value of δH obtained in this way (0.018 Oe) is in good agreement with δH calculated from Eq. (2). This equation gives $\delta H = 0.02$ Oe for $d = 15$ Å and $\Delta H = 2.5$ Oe.

The value $t_{\mathrm{p}} \approx T_{2\mathrm{e}} = 1.2 \cdot 10^{-7}$ s corresponds to a spin packet width ξ 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 ξ considerably larger and the value of 0.5 Oe is therefore not unreasonable.

T_{pex} for one watt calculated with the $E - H_1^2$ curve agrees reasonably well with the value calculated from the experimental values of s for one watt and $T_{1\mathrm{n}}$ at 290 °K using the expression $T_{\mathrm{pex}} = (N/n) \cdot T_{1\mathrm{n}}/(s+1)$ [Eqs. (1 b) and (1 c)]. In this way one obtains $3.4 \cdot 10^{-8}\, s$ ($T_{1\mathrm{n}} = 2$ sec, $s = 2000$ for 1 watt).

T_{P} at 290 °K

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

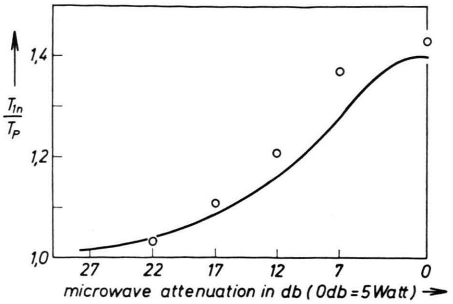

Fig. 6. The experimental values of $T_{1\mathrm{n}}/T_{\mathrm{P}}$ (circles) as a function of the microwave power at 290 °K in single crystals of CaF$_2$ containing H atoms, compared with $T_{1\mathrm{n}}/T_{\mathrm{P}}$ calculated from the experimental values of E, $T_{1\mathrm{n}}$ and the Eqs. (13) and (14) (solid line).

$E_{\max}$ at 80 °K

At 80 °K Eqs (17) and (18) must be applied since $T_{1\mathrm{e}}$ ($3 \cdot 10^{-3}$ s) is larger than $t_{\mathrm{r}} = T_{2\mathrm{e}}/\tau$ for all "polarizing" electrons (with $-\Delta_{\mathrm{L}} < \Delta < +\Delta_{\mathrm{L}}$). We defined a "polarizing" centre as a paramagnetic centre which fulfils the condition $T_{\mathrm{ff}} > t_{\mathrm{r}}$ and which has therefore in our case a value of τ larger than $T_{2\mathrm{e}}/T_{\mathrm{ff}} = 1.2 \cdot 10^{-7}/6 \cdot 10^{-4} = 0.2 \cdot 10^{-3}$. Paramagnetic centres which fulfil $T_{1\mathrm{e}} > t_{\mathrm{r}} = T_{2\mathrm{e}}/\tau$ have values of τ larger than $T_{2\mathrm{e}}/T_{1\mathrm{e}} = 1.2 \cdot 10^{-7}/3 \cdot 10^{-3} = 0.4 \cdot 10^{-4}$. $T_{1\mathrm{e}}$ is thus larger than t_{r} for all "polarizing" electrons.

In Eq. (17) we can neglect both T_{pex}/τ, for sufficiently strong microwave power, and T_{ff}/n_1 ($= 6 \cdot 10^{-4}/400 = 1.5 \cdot 10^{-6}$ s). We get then for $E_{\max}$ with $G(0) \cdot \Delta H_{\mathrm{e}} \approx 1$:

$$E_{\max} = \frac{(2\, \alpha\, N\, \Delta_{\mathrm{L}}/n\, T_{1\mathrm{e}}\, \Delta H_{\mathrm{e}}) \cdot (\Pi_0/P_0) \cdot T_{1\mathrm{n}} + 1}{(2\, \alpha\, N\, \Delta_{\mathrm{L}}/n\, T_{1\mathrm{e}}\, \Delta H_{\mathrm{e}}) \cdot T_{1\mathrm{n}} + 1}. \tag{22}$$

In order to calculate $E_{\max}$ we must determine Δ_{L}. Paramagnetic centres have in our case a value of Δ_{L} when τ 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 $\Delta_{\mathrm{L}} = \pm 3\, \xi$ ($\delta H = 0.018$ Oe and the spin packet width ξ is 0.5 Oe). The width of the "polarizing" region at 80 °K is then equal to $2\, \Delta_{\mathrm{L}} = 6\, \xi = 3$ 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 ΔH_{e} instead of $2\, \Delta_{\mathrm{L}}$.

We then obtain $E_{\max} = 7.5$ using the following values $\alpha = 1/11$, $N = 1.7 \cdot 10^{18}$ c/cm^3, $\Pi_0/P_0 = 700$, $T_{1\mathrm{n}} = 9$ s, $n = 5 \cdot 10^{22}$ k/cm^3 and $T_{1\mathrm{e}} = 3 \cdot 10^{-3}$ s. This value of $E_{\max}$ 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_{max} should be much higher.

Modulation effect

The importance of the modulation effect was already studied in a previous paper[1]. The effect could be explained, but much too large a value of δH had to be chosen in order to fit the experimental curve.

We will now investigate whether, at 290 °K, the experimental $E_{mod}/E - \nu_m$ 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 nominators of the last equation

$$\frac{E_{mod}}{E} = \frac{(1/T_a'/\tau')}{(\delta H/\Delta H_e)\cdot(1/T_a)} \cdot \frac{(\alpha\, N\, \delta H\, n_1/n\, T_a\, \Delta H_e)\cdot T_{1n}+1}{(\alpha\, N\, n_1/n\, T_a'/\tau')\cdot T_{1n}+1}. \tag{23}$$

T_a' and τ' are here the values of T_a [Eq. (15)] and $\tau \approx t_p/t_r$ where t_p and t_r are replaced by

$$t_p' = \frac{2}{\pi}\frac{\delta H}{2\,H_m}\cdot\frac{1}{2\,\nu_m}$$

$$\text{and} \quad t_r' = \frac{1}{2\,\nu_m} \quad \text{for} \quad \delta H \ll H_m\,.$$

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 [$T_{a,\min} = T_{1e}\, n_1/(1+T_{1e}/t_p) = 1.2\cdot 10^{-7}\cdot n_1$ sec]. We get:

$$\frac{E_{mod}}{E} = \frac{\Delta H_e}{\delta H}\cdot 1{,}6\cdot 10^{-7}\,\tau'\,\frac{T_{pex}+T_{1e}\,A'}{(T_{pex}+T_{1e})\,T_{pex}}\,. \tag{24}$$

The theoretical $E_{mod}/E - \nu_m$ curve [Eq. (24)] matches the experimental points very well, if we choose the parameters δH and T_{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 δH and T_{pex} calculated from the experimental $E - H_1^2$ curve (0.018 Oe and $6\cdot 10^{-8}$ sec respectively) and with δH calculated from Eq. (2).

Acknowledgements

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