Experimental Effects of R. F. Irradiation on N. M. R. Lines in Solids

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In this paper measurements about the steady state of both Zeeman and dipolar energies of a spin system submitted to r. f. irradiation are presented. These experiments were performed in order to provide a quantitative check of the existing theories. Two samples are investigated, polycrystalline benzene in which relaxation is caused by molecular motions and a monocrystal of $CaF_2+0.01\%$ Ce^{+++} impurities. For both samples the regions of extreme narrowing and of large T_{1Z}/T_{1D} ratio are investigated. The results are discussed in terms of Provotorov's and Redfield's theories. While in the extreme narrowing region fairly good agreement is obtained some restriction to the Provotorov theory is observed in the region of long correlation times.

Introduction

Due to the strong dipolar interactions between nuclear spins, magnetic resonance in solids is a good deal more complicated than in liquids. Before 1962, only two situations could be treated theoretically, namely the cases of very weak [1] or very strong r. f. irradiations [2]. In the very weak (strong) irradiation case the rate of transitions due to the r. f. field is small (large) as compared to the various characteristic rates of energy exchange between the spin system and the lattice. In simple cases (one spin species with only dipolar interactions in high external field) these rates can be described by two relaxation times T_{1Z} and T_{1D} corresponding respectively to exchange of Zeeman energy or of dipolar energy with the lattice. The basic theory for the weak irradiation case was given by BPP [1]. The interpretation of the behaviour of spin systems under strong saturation was developed by Redfield [2] who introduced the hypothesis of a spin temperature for the whole rotating frame hamiltonian. Redfield's theory has been extensively tested.

In 1962, PROVOTOROV [3] derived a theory which covers the intermediate saturation region provided the irradiation field H_1 be small compared to the local field H_L. Experimentally, this condition is not a limitation since because of their long relaxation time, nearly all solids are well saturated even in the region $H_1 \ll H_L$.

While the Provotorov theory is now frequently used to explain experimental data on solids no direct experimental check of the derived equations exists. This work aims to fill the gap. Two materials are investigated: A crystal of CaF_2 doped with Ce^{+++} ions and a sample of polycrystalline benzene. The samples were chosen because of their very different relaxation mechanisms (impurity relaxation via spin diffusion in the case of CaF_2 and relaxation due to molecular reorientation for C_6H_6). In both cases the extreme narrowing, as well as the long correlation time region were investigated by variation of the temperature. The paper is subdivided in the following way: A short review of the Provotorov and Redfield theories is first given in order to introduce the relations pertinent to the interpretation of measurements. The experimental technique used to measure the various quantities of interest is then described. Finally results are presented with discussion.

Steady State Values of Zeeman and Dipolar Energies under R. F. Irradiation

A) Case of Weak Irradiation

If the radio frequency field is small compared with the local fields ($\mathrm{Tr}\,\mathcal{H}_{\mathrm{r.f.}}^2 \ll \mathrm{Tr}\,\mathcal{H}'^2$, where $\mathcal{H}_{\mathrm{r.f.}}$ is the r.f. Hamiltonian and $\mathcal{H}'$ the secular part of the dipolar interactions) the steady state values of Zeeman and dipolar energies under irradiation, E_Z^{irr} and E_D^{irr}, are given by PROVOTOROV's theory [3, 4] as:

$$\frac{E_Z^{\mathrm{irr}}}{E_0} = \left(\frac{\Delta^2}{\nu_L^2} + \frac{\tau}{T_{1D}}\right) \Big/ \left(\frac{T_{1Z}}{T_{1D}} + \frac{\Delta^2}{\nu_L^2} + \frac{\tau}{T_{1D}}\right) \qquad (1\,a)$$

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$$\frac{E_{\mathrm{D}}^{\mathrm{irr}}}{E_0} = -\frac{\nu_{\mathrm{L}}}{\nu_0} \cdot \frac{\Delta}{\nu_{\mathrm{L}}} \Big/ \left(\frac{T_{1\mathrm{Z}}}{T_{1\mathrm{D}}} + \frac{\Delta^2}{\nu_{\mathrm{L}}^2} + \frac{\tau}{T_{1\mathrm{D}}} \right) \qquad (1\,\mathrm{b})$$

where: $\Delta = \nu - \nu_0$, ν being the irradiation frequency and ν_0 the Larmor frequency.

ν_{L} is the local frequency. In the case of only one spin species and only dipolar interactions, ν_{L}^2 is simply related to the second moment of the absorption line:

$$\nu_{\mathrm{L}} = (1/\sqrt{3}) \cdot (1/2\,\pi) \cdot \langle \Delta\omega^2 \rangle^{1/2} .$$

$1/\tau \equiv W = \gamma^2 H_1{}^2 \pi f(\omega)$, where H_1 is the amplitude of the r.f. field and $f(\omega)$ the normalized line shape. τ is the characteristic time at which the Zeeman energy goes to zero under an irradiation in the centre of the line and in absence of spin lattice relaxation. E_0 is the Zeeman energy in complete equilibrium with the lattice. Equations (1 a) and (1 b) are valid for weak as well as for strong saturation of the absorption line provided $H_1 \ll H_{\mathrm{L}}$.

It is also worth mentioning here, that these equations rely on the following hypothesis:

The various spin-lattice relaxation mechanisms are considered as slow enough for internal equilibrium inside the dipolar and Zeeman subsystems not to be disturbed by the lattice.

The total rates of changes of the Zeeman and dipolar energies can be written simply as sums of two terms, one containing the effect of the r.f. field only and one the effect of spin lattice relaxation only.

$$\frac{\mathrm{d}}{\mathrm{d}t} E_{\mathrm{Z,\,D}} = \left(\frac{\partial E_{\mathrm{Z,\,D}}}{\partial t} \right)_{\mathrm{r.f.}} + \left(\frac{\partial E_{\mathrm{Z,\,D}}}{\partial t} \right)_{\mathrm{s.l.}} . \qquad (2)$$

In the case of very weak H_1 ($\tau/T_{1\mathrm{D}} \gg \Delta^2/\nu_{\mathrm{L}}^2$) the well known result of BPP[1] is obtained from (1)

$$\frac{E_{\mathrm{Z}}^{\mathrm{irr}}}{E_0} = \frac{1}{1 + \gamma^2 H_1{}^2 \pi f(\omega)\, T_{1\mathrm{Z}}}$$

and the dipolar energy approaches zero.

B) Case of Strong Irradiation

If the radio frequency field is large, $\tau \ll T_{1\mathrm{Z}}$ and $T_{1\mathrm{D}}$, the behaviour of the spin system was described by Redfield under the assumption of a unique spin temperature for the whole Hamiltonian in the rotating frame. The resulting relations for the Zeeman and dipolar energies under a steady state of irradiation are:

$$\frac{E_{\mathrm{Z}}^{\mathrm{irr}}}{E_0} = \frac{\Delta^2}{\nu_{\mathrm{L}}^2} \Big/ \left(\frac{T_{1\mathrm{Z}}}{T_{1\mathrm{D}}} + \frac{\Delta^2}{\nu_{\mathrm{L}}^2} + \frac{T_{1\mathrm{Z}}}{T_{1\mathrm{x}}} \frac{\nu_1^2}{\nu_{\mathrm{L}}^2} \right), \qquad (3\,\mathrm{a})$$

$$\frac{E_{\mathrm{D}}^{\mathrm{irr}}}{E_0} = -\frac{\nu_{\mathrm{L}}}{\nu_0} \cdot \frac{\Delta}{\nu_{\mathrm{L}}} \Big/ \left(\frac{T_{1\mathrm{Z}}}{T_{1\mathrm{D}}} + \frac{\Delta^2}{\nu_{\mathrm{L}}^2} + \frac{T_{1\mathrm{Z}}}{T_{1\mathrm{x}}} \cdot \frac{\nu_1^2}{\nu_{\mathrm{L}}^2} \right) \qquad (3\,\mathrm{b})$$

where $T_{1\mathrm{x}}$ is the relaxation time of the Zeeman energy developed by H_1 in the rotating frame (H_1 is assumed to be along the x-direction in that frame) and $2\,\pi\,\nu_1 = \gamma\,H_1$. Equations (3) were given by Redfield for the extreme narrowing region only ($T_{1\mathrm{Z}} = T_{1\mathrm{x}}$) and later extended (Ref. [5]) to the region of long correlation times ($\tau_{\mathrm{c}} > 1/\omega_0$).

Since these equations imply a good contact between Zeeman and dipolar subsystems they are not valid when the effective field becomes large compared to the local field (large H_1 values near resonance, or large Δ values). A necessary condition for their validity is, however, that the absorption be saturated.

Equations (1) and (3) are easily seen to be equivalent for ν_1 values large enough to saturate the absorption line ($\tau < 1/T_{1\mathrm{Z}}$) but small compared to ν_{L}. When ν_1 becomes of the order of ν_{L}, the curves described by Eqs. (3) broaden. This broadening is of course not contained in the Provotorov theory in which the effect of relaxation along the H_1 direction is simply omitted. However, as we shall see in the experimental results this H_1 broadening becomes very important when the ratio $T_{1\mathrm{Z}}/T_{1\mathrm{x}}$ is very large.

In the case of a large effective field (Δ or $\nu_1 > \nu_{\mathrm{L}}$), when the contact between the Zeeman and dipolar system can be neglected, the situation can be described by modified Bloch-equations[2] with an extra relaxation time in the direction of the H_1-field, $T_{1\mathrm{x}}$.

Experimental

A) Measurement of Zeeman and dipolar relaxation times

$T_{1\mathrm{Z}}$ and $T_{1\mathrm{D}}$ were measured by conventional pulse techniques. For the Zeeman relaxation time two 90°-pulses were used, and the amplitude of the signal following the second pulse was plotted as a function of the time interval between them. In order to measure the dipolar relaxation time $T_{1\mathrm{D}}$, the spin system was first prepared in a state of low dipolar and infinite Zeeman temperature. A 45°-pulse was then applied, and the heighth of the dipolar free induction decay was plotted as a function of the time interval between the last pulse and the second preparation pulse. For more details, the reader is referred to the work of JEENER et al.[6] who proposed the method.

B) Measurement of $T_{1\mathrm{x}}$

We have measured $T_{1\mathrm{x}}$ in the centre of the n.m.r.-line with the pulse sequence given in Fig. 1: A 90°-

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pulse in the y-direction brings the magnetization (which was originally in thermal equilibrium) into the x-direction. Immediately after the 90°-pulse a radio frequency pulse of amplitude H_1, frequency ν_0 (like the 90°-pulse) and of duration t_1 is applied along the x-direction. For each H_1 the amplitude of the free induction decay after the second pulse is plotted against the duration t_1. For small H_1 values a first rapid decay in a time of a few T_2 (which is due to the exchange between Zeeman and dipolar energy) is not considered, while we use the subsequent exponential decay for the T_{1x} determination. In order to maintain the magnetization aligned along x during the decay, H_1 is always large enough to saturate the absorption signal.

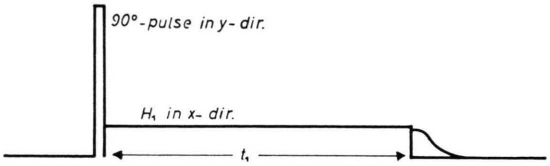

Fig. 1. Pulse sequence used for the T_{1x} measurements.

C) Measurements of E_Z^{irr} and E_D^{irr}

In order to check the Provotorov theory the pulse sequence shown in Fig. 2 was used. The first pulse, of amplitude H_1 and frequency ν at a distance Δ from the centre of the n.m.r.-line, lasts for a time t_2 long enough for a stationary state ($t_2 \gg T_{1Z}$) to be reached. After a time of several T_2 following this first irradiation pulse, a short 45°-pulse in the x-direction was given at the exact Larmor frequency ($\nu_0 = 15$ Mc/s). The heights of the Zeeman (y-channel) and dipolar (x-channel) free induction decays, properly separated by orthogonal phase detection, were recorded as a function of H_1 and Δ. The H_1 field was calibrated by measuring the time required for a 180°-pulse in a liquid sample. The irradiation and observing pulses were fed through two orthogonal coils.

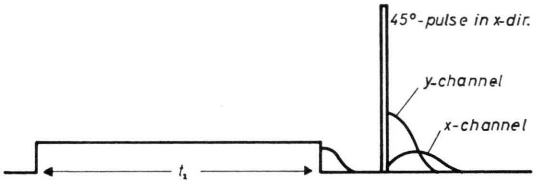

Fig. 2. Pulse sequence used for the measurement of Zeeman- (y-channel) and dipolar (x-channel) free decays after a r.f. irradiation.

H_1 could be varied from 0 up to 1.5 gauss approximately. ν was changed in steps by means of a Schlumberger frequency synthesizer.

Results and Discussion

A) Short Correlation Times

(a) Benzene

Figure 3 represents the experimental results, E_Z^{irr}/E_0 and E_D^{irr} against Δ, obtained for C_6H_6 in a region of temperature where the extreme narrowing condition is fulfilled. The quantity E_D^{irr} is in relative units. The quantity effectively plotted is the ratio of dipolar to Zeeman amplitudes of the free decays following the 45°-pulse taken at the time corresponding to the maximum of the dipolar signal.

The six dotted lines in this figure correspond to small H_1 values. They are theoretical plots of the Eqs. (1). τ was calculated as a function of Δ and H_1 by assuming a Gaussian line shape, a hypothesis well supported by the Gaussian behaviour of the free decay. One value of τ for $\Delta = 0$ and $H_1 = 0{,}016$ G was adapted to the corresponding experimental point. This adapted τ was about 25% different from the calculated one. This discrepancy could be due to errors in the H_1 calibration and to insufficient know-

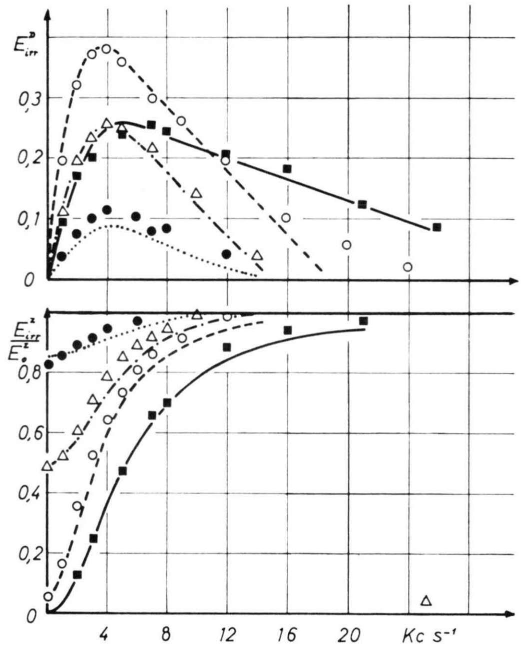

Fig. 3. Plot of the Zeeman and dipolar energies for benzene as functions of Δ for different irradiation amplitudes (□ ——— $H_1 = 1.32$ G; ○ – – – – $H_1 = 0.066$ G; △ —·—·—·— $H_1 = 0.016$ G; ● ········ $H_1 = 0.0066$ G). The measurements were performed under the following conditions: $T = 226$ °K; $T_{1Z} = 0.25$ s; $T_{1D} = 0.149$ s; $\langle \Delta\nu^2 \rangle^{1/2} = 4.58$ kc/s.

ledge of the exact n.m.r. line shape in the wings. The constant factor between the amplitude of the dipolar free precession decay and dipolar energy was also experimentally determined from the maximum of the dipolar curve with $H_1 = 0{,}016$ G.

By comparing the theoretical lines with the experimental points, it is clear from Fig. 3 that the agreement with the Provotorov theory is good. The small observed deviations are most probably due to the fact that the line, especially in the wings is not exactly a Gaussian.

The experimental behaviour at a large H_1 value ($H_1 = 1{,}32$ G) was interpreted with Eq. (3) (solid line) and with $T_1 = T_{1\text{x}}$ – a reasonable assumption for the extreme narrowing region. The agreement with theory is good. The decrease in amplitude of the maximum dipolar signal is due to the contribution of the H_1 broadening, H_1 being here of the same order as H_L.

(b) Calcium Fluoride

Figure 4 shows the experimental results concerning CaF_2. One τ value corresponding to $\Delta = 0$ and $H_1 = 0{,}039$ G was adapted. Here again the six dotted lines corresponding to low H_1 values were calculated from Eqs. (1) using the line shape measurements of Bruce[7] belonging to our orientation of the crystal ($H_0 \parallel [110]$).

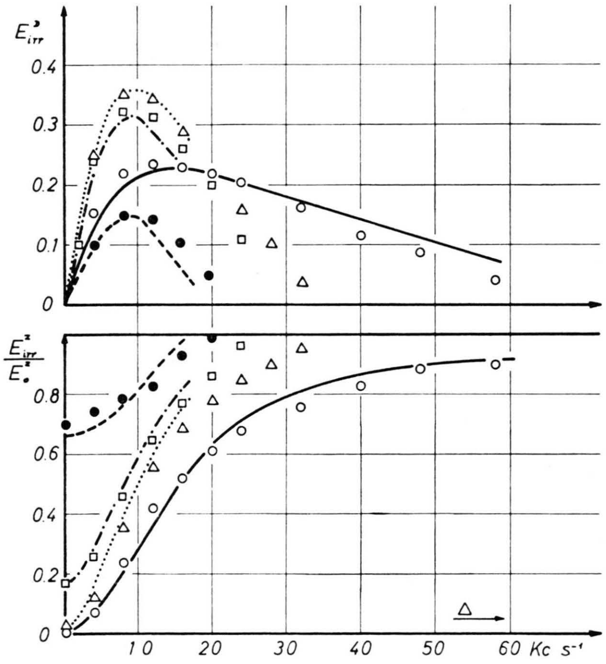

Fig. 4. Same as Fig. 3 for $CaF_2 + 0.01\%$ Ce^{+++} with the [110] axis parallel to H_0 (○ ——— $H_1 = 1.23$ G; △ ········ $H_1 = 0.13$ G; □ —·—·—·— $H_1 = 0.039$ G; ● – – – – – – $H_1 = 0.013$ G). $T = 67$ °K; $T_{1\text{Z}} = 0.28$ s; $T_{1\text{D}} = 0.1$ s; $\langle \Delta\nu^2 \rangle^{1/2} = 9.5$ kc/s.

In the region $\Delta > 16$ kc/s the theoretical curves are not drawn since no accurate experimental information on the line shape exists for larger Δ values. The calculated dotted lines are, as far as they could be used, a little narrower than the measured ones.

The solid curves, corresponding to $H_1 = 1{,}32$ G are theoretical plots of the Eqs. (3) with the following values of the parameters:

$$T_{1\text{Z}}/T_{1\text{D}} = 2{,}8 ; \qquad T_{1\text{Z}}/T_{1\text{x}} = 6 .$$

$T_{1\text{x}}$ was also determined and found to be of the same order as $T_{1\text{Z}}$. This experimental determination of $T_{1\text{x}}$ is in good agreement with a simple calculation[5] according to which the ratio $T_{1\text{Z}}/T_{1\text{x}}$ should be of the order of 7/6 in the extreme narrowing region for relaxation by paramagnetic impurities. It is, on the other hand, clear that a larger value of $T_{1\text{Z}}/T_{1\text{x}}$ of the order 5 or 6 is required to describe the decrease in the maximum dipolar signal amplitude of the $H_1 = 1{,}32$ G curve. This decrease comes from the growing importance of the term

$$(T_{1\text{Z}}/T_{1\text{x}}) \cdot (\nu_1^2/\nu_\text{L}^2)$$

in the denominator of Eq. (3 b). We think that one reason for the discrepancy could be a variation of the ratio $T_{1\text{Z}}/T_{1\text{x}}$ with Δ. However, the real reason for the discrepancy, which is still more important at low temperature ($\omega_0 \tau_\text{c} > 1$), is not clear.

B) Long Correlation Times

(a) Benzene

In Fig. 5 we have plotted the results for C_6H_6 at 120 °K where the ratio $T_{1\text{Z}}/T_{1\text{D}}$ was measured[8] to be $5.5 \cdot 10^3$. This is a region where the correlation time τ_c is still short compared to $1/\gamma H_\text{L}$ and a weak collision theory for relaxation can still be applied. In this picture the solid curves are simply drawn through the experimental points while the dotted curves are theoretical ones. In a comparison of these results with those obtained for benzene, in the region of extreme narrowing, several new and remarkable aspects have to be considered.

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[8] R. Van Steenwinkel, Z. Naturforsch. **24 a**, 1526 [1969].

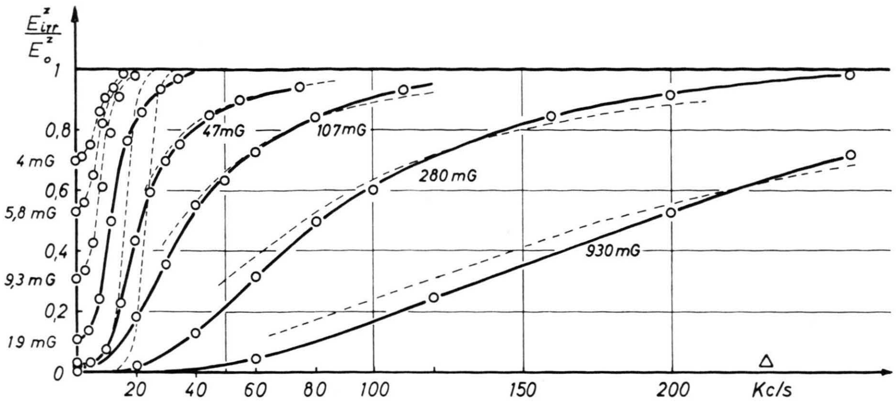

Fig. 5. Plot of the Zeeman energy for benzene as a function of Δ and for different irradiation amplitudes: ($T=120$ °K; $T_{1Z}=1{,}1$ s; $T_{1D}=0.2$ ms; $\langle\Delta\nu^2\rangle^{1/2}=5.7$ kc/s).

i) The dipolar signal is unobservably small.

ii) The lines are extremely broad (for instance, an irradiation with $H_1=1$ G at 200 kc/s from the centre results in a steady state magnetization which is 1/2 of its full value).

iii) It seems that the domain of validity of the Provotorov theory is now limited to very small values of H_1 ($H_1 \leqq 1/50\, H_L$).

We now discuss these various points:

i) The absence of the dipolar signal is a rather trivial consequence of the large T_{1Z}/T_{1D} ratio, as can be checked on Eqs. (1) and (3).

ii) Clearly the width of the saturation curves cannot be explained by the smallness of T_{1D}. Far from the centre of the line (for $\Delta > 40$ kc/s) the "effective" Zeeman Hamiltonian is large compared to the dipolar one and, as already mentioned before, the Redfield hypothesis of a unique spin temperature for both subsystems in the rotating frame breaks down. Roughly speaking the thermal contact between both subsystems slows down as

$$\exp(c\cdot H^2_{\text{eff}}/H^2_L) \qquad (\text{with } c\approx 1)$$

and is thus very weak for an $H_{\text{eff}} > 10\, H_L$. On the other hand, far from the centre, the effective Zeeman Hamiltonian is in fact the main part of the total Hamiltonian. This consideration suggests that the behaviour of the magnetization far from the centre might be given simply by some modified Bloch equations like those proposed by Redfield:

$$\left(\frac{\partial M_x}{\partial t}\right)_l = -M_x/T_{1x}\,, \tag{5 a}$$

$$\left(\frac{\partial M_y}{\partial t}\right)_l = -M_x/T_2\,, \tag{5 b}$$

$$\left(\frac{\partial M_z}{\partial t}\right)_l = -(M_z - M_0)/T_{1Z} \tag{5 c}$$

where $(\partial M_x/\partial t)_l$ means the rate of change of the x-component of magnetization in the rotating frame due to spin-lattice interactions only. The use of such a set of equations, together with the strong saturation condition ($M_y=0$) results in Eq. (3 a) where the term (T_{1Z}/T_{1D}) is set equal to zero.

Such an interpretation is, at least qualitatively, confirmed by our experimental results. In Fig. 5, the dotted lines for $H_1 \geqq 47$ mG are drawn according to this theoretical hypothesis. The values of T_{1Z}/T_{1x} used for the interpretation are given in Table 1.

Table 1.

H_1	930 mG	280 mG	107 mG	47 mG
T_{1Z}/T_{1x}	2050	4040	6250	8960

A direct measurement of the T_{1Z}/T_{1x} ratio was performed at an H_1 value of about 1 G giving $T_{1Z}/T_{1x}\approx 2300$. While affected by large experimental error this value compares rather well with the value (2050) used to fit the experimental curves. For smaller H_1 fields experimental errors in the determination of T_{1x} are still larger but within these errors they confirm the H_1 dependence of T_{1Z}/T_{1x} used in the interpretation. We conclude that the broadness of the curves is to be attributed essentially to the shortness of T_{1x}. This result seems to give at least some experimental justification for Eq. (5), even for H_1 fields small compared to the local fields, provided one is far enough from resonance.

iii) Due to the lack of informations about the line shape in the wings of the absorption curve a comparison of the experimental results for small H_1 with Provotorov's theory is difficult. For very small H_1 values (4; 5.8 and 9.3 mG) the agreement with Eqs. (1) is excellent.

In Fig. 5 the theoretical curves corresponding to $H_1 = 47$ mG and $H_1 = 280$ mG are also plotted. Since these values are still small compared to H_L, one should expect good agreement with the predictions of Eqs. (1). The large deviations observed can be interpreted in two ways: Either the Gaussian approximation for the line shape is completely wrong far from resonance, or Eq. (1 a) is doubtful for large T_{1Z}/T_{1D} values and intermediate H_1-fields (still smaller however than H_L).

We think that the latter argument is the correct one. We have already seen in the extreme narrowing region that the effect of H_1-broadening is appreciable, giving rise to the decrease in the maximum of the dipolar curve in Fig. 3 for $H_1 = 0{,}93\ \text{G} \approx H_L$. For the actual case of very large T_{1Z}/T_{1x}-ratios this H_1-broadening begins already (Fig. 5) for

$$\nu_1 \approx \nu_L \cdot \sqrt{T_{1x}/T_{1Z}}\,.$$

This more restrictive condition comes from the fact that the actual relaxation rate of the magnetization is not simply given by the Zeeman relaxation time T_{1Z} as assumed by Provotorov, but by a combination of T_{1Z} and T_{1x} as described in Ref. [5]. It is clear, however, that in the extreme narrowing region the condition of Provotorov coincides with the above one.

(b) Calcium Fluoride

Finally, in Fig. 6 are collected the experimental results concerning CaF$_2$ in a region of temperature where the ratio T_{1Z}/T_{1D} is 80. We will not discuss at length these results since new experiments have to be done in order to clarify the observed behaviour.

Some characteristic features of these results can be summarized as follows: For all H_1 values the experimental curves are considerably broader than predicted by Eqs. (1 a) and (3 a). The three dotted lines corresponding respectively to 12; 20 and 50 mG are drawn using formula (1) and the data of BRUCE [7] on the line shape. The deviation from the measurements is large and far beyond possible experimental errors.

The experimental curves corresponding to .2, .4 and 1 G if interpreted with formula (3 a) yield a T_{1Z}/T_{1x} ratio in the range of 1000 to 5000 in strong disagreement with the direct T_{1x} measurement which gives $T_{1Z}/T_{1x} \approx 100$ or less.

This behaviour most probably comes from an important contribution of the nuclei in the direct neighbourhood of the impurities. At this low temperature the Ce-ions have a rather long relaxation time and they are responsible for a large local field in their vicinity giving a non zero susceptibility very far from the centre of the line. Such an explanation will be checked by further experiments on the temperature and Ce-concentration dependance of the results.

Conclusion

This experimental work concerning the effect of r.f. irradiation on a solid n.m.r. line has shown that the behaviours of Zeeman and dipolar energies obey rather well the existing theories, at least in the re-

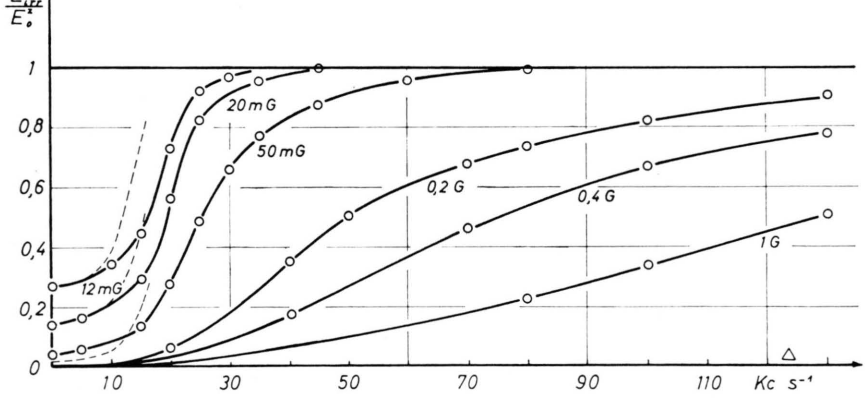

Fig. 6. Same as Figure 5 for CaF$_2$ +0.01% Ce^{+++} with the [110] axis parallel to H_0 (T=6.1 °K; T_{1Z}=1.68 s; T_{1D}=20.6 ms; $\langle \Delta\nu^2\rangle^{1/2}$=9.5 kc/s).

gion of extreme narrowing. Some small deviations are, however, observed in CaF_2 when spin lattice relaxation takes place by the presence of paramagnetic impurities rather than by molecular motions. In the region of large T_{1Z}/T_{1D} ratios a limitation of Provotorov's theory to very small H_1 values ($H_1 < H_L \sqrt{T_{1x}/T_{1Z}}$) is observed. On the other hand the validity of modified Bloch equations is at least qualitatively confirmed in the case of C_6H_6. The experiment shows that these equations are not only valid in the limit $H_1 > H_L$ but better when $H_{eff} > H_L$ a much less restrictive condition.

In the case of CaF_2 the broadening of the experimental curves is considerably larger than would be expected from the T_{1Z}/T_{1D} ratio. This result which is probably due to the complicated relaxation situation around the paramagnetic impurities is not completely understood.

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