

The Enhanced Longitudinal Susceptibility Effect (ELSE) and its Applications in Magnetic Resonance

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I. INTRODUCTION

A. Subject and Structure of the Paper

In studies of spin dynamics and relaxation in solids the spin-temperature concept is widely used, according to which the relatively weak spin-spin interaction is considered as a separate quasi-equilibrium subsystem

("the spin-spin reservoir"), possessing its own independent spin temperature T_{SS} .

This concept was developed theoretically and experimentally verified both for nuclear and, after some delay, for electronic spin systems, resulting in the discovery of many interesting effects concerned with saturation of the magnetic resonance, cross relaxation, spin-lattice relaxation, dynamic polarization of nuclei, and others. See, e.g., the original papers by Anderson and Hartmann (1), Provotorov (2), Jeener et al (3), Rodak (4), the reviews (5-9), as well as the monograph by Goldman (10). However, in spite of such a success of the spin-temperature theory our understanding on a quantitative level of the various physical processes occurring in paramagnetic solids is still far from complete. This may be related to the fact that the spin-spin reservoir, despite playing a significant (and, sometimes, decisive) role in all above-mentioned phenomena, manifests itself mostly in an indirect way, through some small changes in the resonance line shape and so on. As a consequence, the accurate measurement of the spin-spin temperature T_{SS} is a rather difficult task, especially in EPR, and it is just this fact that explains why the experimental verification of the " T_{SS} -concept" in electron spin systems has taken so much effort (6).

By contrast, the enhanced longitudinal susceptibility effect (ELSE), which this review is concerned with, yields the most immediate information on the spin-spin reservoir and so enables one to gain a more penetrating insight into spin dynamics and relaxation in solids.

According to its name, ELSE is a sharp increase in the

low-frequency longitudinal magnetic susceptibility; it is caused by cooling the spin-spin reservoir with the aid of the asymmetrical saturation of the magnetic resonance. ELSE was theoretically predicted (11) in 1973 and soon afterwards experimentally observed (12). On further study (13-20), this effect was found to be not only interesting from the purely physical point of view, but also quite useful as an effective and convenient tool for the investigation of spin systems, both electronic and nuclear.

In Section I. B we begin with a brief historical introduction, where advantages and disadvantages of two well-known techniques, the older "parallel-field" and the magnetic resonance methods, are compared. Then, in section II, the concept and elementary theory of ELSE are given, along with outlines of the appropriate experimental setup designed for producing and observing the enhanced susceptibility. The more rigorous theory is put off until Section IV, while in Section III some experimental examples of ELSE are presented with only a qualitative physical interpretation. This arrangement is due to our intention to give the clearest explanation of the physical meaning, avoiding complicated calculations wherever possible.

Finally, in Section V we present some experimental data on spin dynamics and relaxation obtained by means of ELSE. This deals with features and behavior of the electron spin-spin reservoir in dilute paramagnetic crystals (Sections V. B, C, D), but some other applications of ELSE are described as well, including a study of low-frequency nuclear magnetic resonance in the rotating reference frame (Section V. E). Here, a new approach to high-resolution NMR in solids is suggested (18, 19, 21). Our purpose in this part of the paper is not to describe comprehensively the subjects under consideration, but rather to demonstrate the potentialities of the ELSE technique in studies of spin systems.

B. Longitudinal Susceptibility and Magnetic Resonance

In the 1930s, long before the discovery of paramagnetic resonance, a method was developed for the investigation of paramagnetic relaxation. Frequently called the "parallel-field" method, it was initiated by Dutch physicists, especially Gorter's group in Leiden (22).

In the classical variant of the "Leiden" method, an alternating magnetic field $he^{i\omega t}$ is applied to a paramagnetic sample placed in a constant magnetic field $H_0 \gg h$ parallel to the alternating field, and the magnetic susceptibility

$$\chi(\Omega) = \frac{\partial M_z}{\partial H_z}$$

is measured at relatively low frequencies (up to 10^6 - 10^7 Hz). (M_z is the projection of the magnetic moment of the sample on the H_0 direction.)

If the longitudinal relaxation of the magnetic moment is described by the simple equation of the type

$$\frac{\partial M_z}{\partial t} = - \frac{M_z - M_{z0}}{\tau} \quad (1)$$

where M_{z0} is the equilibrium value of M_z and τ is the relaxation time, then the longitudinal susceptibility is given by the well-known expression (22):

$$\chi(\Omega) = \frac{\chi_0}{1 + i\Omega\tau} \quad (2)$$

where $\chi_0 = M_{z0}/H_0$ is the static susceptibility.

Usually the real (χ') and imaginary ($-\chi''$) parts of $\chi(\Omega)$ are experimentally separated. They are proportional to the dispersion and absorption signals, respectively, at the frequency Ω :

$$\chi'(\Omega) = \chi_0 \frac{1}{1 + \Omega^2\tau^2} \quad (3)$$

$$\chi''(\Omega) = \chi_0 \frac{\Omega\tau}{1 + \Omega^2\tau^2} \quad (4)$$

These expressions are the special case of a more general relation (23):

$$\chi''(\Omega) \propto \Omega J(\Omega) \quad (5)$$

where $J(\Omega)$ is the Fourier transform of the relaxation function $M_z(t)$.

Thus the functions $\chi'(\Omega)$ and $\chi''(\Omega)$ are unambiguously related to the relaxation law, and so the "parallel-field" experiments enable one to determine the relaxation time τ , or in a more general case, a set of relaxation times τ_i .

The Leiden method was regarded in its time as quite fruitful. Thus, it was used to observe for the first time and to study spin-lattice and spin-spin relaxation processes. However, following the discovery and rapid development of magnetic resonance, the low-frequency procedure was pushed into the background, and it is used at present in only two or three laboratories, including the original group in Leiden (see, for example, (24)). This fact is apparently caused by the low sensitivity of the "parallel-field" method as compared to the magnetic-resonance one. Indeed, as one can see from Eq. (2), the $\chi(\Omega)$ value does not exceed the static susceptibility χ_0 , whereas the magnetic-resonance signals are of the order of $\chi_0 H_0 / \Delta H$, where ΔH is the resonance line width. Since usually $H_0 / \Delta H \approx 10^2$ - 10^4 , the gain in sensitivity may reach several orders of magnitude.

On the other hand, the merits of the Leiden method are its high information content concerning the shape of the relaxation function, as well as the possibility of measuring relatively short relaxation times (10^{-7} - 10^{-9} s), which presents difficulties in the magnetic-resonance technique.

For a long time the Leiden method and magnetic resonance were developed "in parallel," being practically independent of one another. ELSE, as we shall show, may be regarded as an attempt to combine them and achieve the advantages of both methods.

II. PHYSICAL GROUNDS OF ELSE

A. Two-Temperature Concept

Initially we will outline briefly the principal ideas of the spin-temperature concept (2, 5, 10) insofar as it is essential in understanding ELSE.

Consider a paramagnetic solid containing spins S (electronic or nuclear) placed in a static external magnetic field H_0 , where the Larmor frequency of the spins is $\omega_0 = \gamma H_0$. Let H_0 be much larger than the local field $H_L \equiv \omega_L/\gamma$ caused by spin-spin interactions (as a rule, these are magnetic dipole-dipole interactions, but in general their origin may be different: exchange, hyperfine, etc.). Then the main term in the Hamiltonian of the spin system is that determined by Zeeman interaction of the spins with the field H_0 :

$$\mathcal{H}_Z = -\omega_0 S^z$$

where S^z is the total projection of the spins on the H_0 direction, whereas the spin-spin interaction is responsible for broadening the energy levels up to the width of the order of ω_L . On the other hand, the spin-spin interaction, being usually much stronger in solids than is the spin-lattice interaction, provides the establishment of the internal quasi-equilibrium in the spin system characterized by the density matrix:

$$\rho = \frac{\exp(-\mathcal{H}_Z\beta_Z - \mathcal{H}_{SS}^0\beta_{SS})}{\text{Tr}\{\exp(-\mathcal{H}_Z\beta_Z - \mathcal{H}_{SS}^0\beta_{SS})\}} \approx \frac{1 - \mathcal{H}_Z\beta_Z - \mathcal{H}_{SS}^0\beta_{SS}}{\text{Tr} 1} \quad (6)$$

where \mathcal{H}_{SS}^0 is the secular (commuting with \mathcal{H}_Z) part of the spin-spin interaction Hamiltonian, and $\beta_Z \equiv 1/kT_Z$, $\beta_{SS} \equiv 1/kT_{SS}$ are the inverse temperatures of two separate energy reservoirs: the Zeeman subsystem and the interaction one, respectively.

The second equality in Eq. (6) is valid in the high-temperature approximation ($\hbar\omega_0 \ll kT_Z$) that will henceforth be assumed. Then, owing to the condition $\omega_0 \gg \omega_L$ that prevents the energy exchange between Zeeman and spin-spin reservoirs, the two subsystems are mu-

tually independent, and their temperatures may differ, in general, from one another (and from the lattice temperature $T_0 \equiv 1/k\beta_0$).

Suppose that the sample is irradiated by the radio-frequency (rf) magnetic field $2H_1 \cos \omega t$ normal to the z-axis and saturating the magnetic resonance with a small detuning:

$$\Delta = \omega - \omega_0$$

Then at $H_1 \ll H_L$ the evolution of the temperatures T_Z and T_{SS} under the action of this field is described by Provotorov's equations (2). According to these equations, such an "off-center" saturation sharply increases $|\beta_{SS}|$ to a value of the order of $\beta_0\omega_0/\omega_L$, i.e., strongly cools the spin-spin reservoir (the β_{SS} value can either be positive or negative, its sign being opposite to that of Δ). At complete saturation, a dynamic equilibrium is established characterized by the relation:

$$\beta_{SS}\Delta + \beta_Z\omega_0 = 0 \quad (7)$$

Formal expressions for the inverse temperatures β_{SS} and β_Z as obtained from Provotorov's equations are given in Section IV. A; here it is sufficient to say that, unless $\Delta = 0$, the β_Z value is *not* equal to zero and depends strongly on the detuning, as can be seen in Eq. (7).

B. Origin of ELSE

Now we estimate the magnitude of the longitudinal susceptibility being measured under saturation conditions. To do this, the susceptibility definition is used:

$$\chi = \delta M_z / \delta H_0$$

where δM_z is the change in longitudinal magnetization caused by a small increment δH_0 to the external field. Recognize, however, that at $\omega = \text{const}$, any increment δH_0 to H_0 results in the corresponding decrement $\delta\Delta = -\gamma\delta H_0$ of the detuning Δ . According to the previous subsection, this leads to a strong change in the Zeeman temperature and, therefore, in the longitudinal magnetization, which is proportional to β_Z , giving rise to an appreciable susceptibility.

As an example, suppose that the resonance line is initially saturated with a detuning $\Delta \approx \omega_L$, so that $M_z \approx M_{z0}/2$ (see below, Eqs. (18) and (19), together with Eq. (7)). Now let H_0 increase by a relatively small amount $\delta H_0 \approx H_L \ll H_0$, leading to a shift of the saturation point from the wing of the line to its center ($\Delta = 0$). As a result, magnetization vanishes, and one gets:

$$\chi = \frac{\delta M_z}{\delta H_0} \approx -\frac{M_{z0}}{2H_L} = -\chi_0 \frac{H_0}{2H_L}$$

That is, the absolute value of the susceptibility exceeds χ_0 by several orders of magnitude. This is just the ELSE.

Note that in the above example the χ value is found to be negative (an increase in H_0 results in decreasing M_z). It is clear that the sign of χ will change if the saturation is performed on the opposite wing of the line, i.e., at $\Delta < 0$. As will be seen shortly, this is related to the proportionality between the enhanced susceptibility and β_{SS} .

There can also exist another, much more trivial mechanism for the susceptibility enhancement, not associated with the spin-spin reservoir at all. Indeed, a strong dependence of M_z on Δ may be caused simply by the dependence of the saturation factor s on the form factor of the resonance line (a similar effect is used, for instance, in measuring spin-lattice relaxation by rapid modulation of the saturation factor (25)). It is clear, however, that this parasitic effect should vanish at strong saturation ($s \gg 1$), whereas the "true" ELSE does exist just in this case.

The physical meaning of ELSE may also be explained in other terms. As is well known, the behavior of the spin system under saturation conditions can be described in the rotating reference frame (RF), which rotates about the z axis at the frequency ω . If $H_1 \lesssim H_L$, a single spin temperature T_{RF} is established in the rotating frame (26). This temperature is equal to T_{SS} and, consequently, is much lower than T_0 .

According to Curie's law, the magnetic susceptibility is inversely proportional to the spin temperature; therefore, the χ value being measured in the rotating frame has to become T_0/T_{SS} times as large. The very essence of ELSE is that the direction of the z -axis is the same both in the rotating and laboratory frames (provided $H_1 \ll H_L$), hence the enhanced susceptibility has to be observed in the laboratory frame as well, by means of the commonly used "parallel-field" method.

Although the foregoing is concerned only with the special case (the susceptibility related to the thermal mixing in the RF, see Section III. C), the proportionality between the enhanced susceptibility and the β_{SS} value is valid in general, for all varieties of ELSE. This important conclusion may be qualitatively explained as follows.

As mentioned above, the imaginary part of the susceptibility, $\chi''(\Omega)$, corresponds to the absorption of the energy of the low-frequency alternating field. Evidently, this absorption must be associated with quantum transitions in some subsystem possessing an appropriate low-frequency energy spectrum. Whatever this subsystem may be (particularly, but not necessarily, it may be formed by the Zeeman energy of the spins in the effective field acting in the RF), this subsystem has to be in strong thermal contact with the spin-spin reservoir whose spectrum falls within the same frequency band, and hence its temperature must be equal to T_{SS} . Since,

on the other hand, the absorption coefficient of the spin system is inversely proportional to its temperature, the $\chi''(\Omega)$ value has actually to be proportional to β_{SS} , and so the cooling of the spin-spin reservoir must lead to an increase of the susceptibility by a factor of T_0/T_{SS} .

C. Outline of the Experimental Setup

It is now appropriate to give a brief description of the apparatus used for producing and observing the enhanced susceptibility. The block diagram is shown in Figure 1.

The sample is placed into the longitudinally oriented low-frequency coil connected with an apparatus for measuring the dispersion and/or absorption signals at frequency Ω — it may be, for instance, a Q -meter or a marginal oscillator (an autodyne). In the case of the electron spin system, the frequency ω of the saturating field falls in the EPR (microwave) band, so the pumping may be accomplished by a resonant cavity or simply by a short-circuited waveguide (Figure 1). In the case of nuclear spins, the NMR saturation may be achieved with the aid of an additional (rf) coil crossed with the low-frequency one. A similar rf coil may also be used in the former case (EPR) if one desires to observe simultaneously the NMR spectrum of the nuclear spins of the host lattice (see Section V. B).

As to the Ω value, the choice of the appropriate frequency range is determined by the nature of the susceptibility to be measured. As seen from Eqs. (2)-(5), the $\chi'(\Omega)$ and $\chi''(\Omega)$ values reach their maxima at $\Omega \leq \tau^{-1}$.

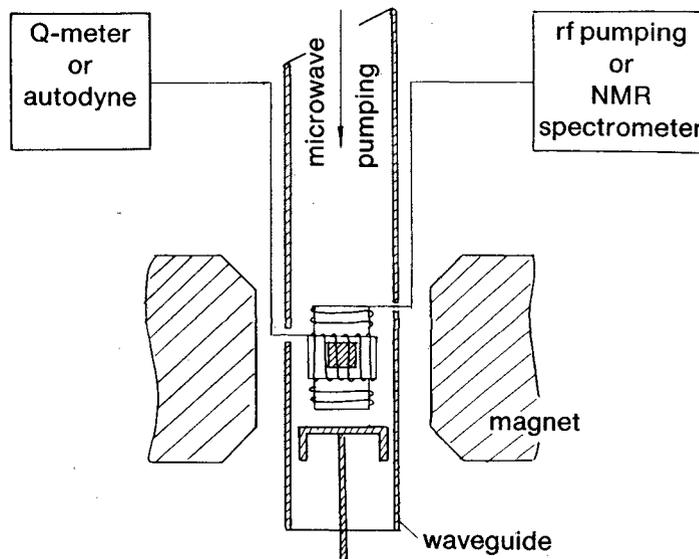


Figure 1. Block diagram of the experimental setup for observing ELSE.

Recognizing that relaxation times can vary from 10^{-6} - 10^{-8} s (electron spin-spin relaxation in low fields) up to 10s or more (nuclear spin-lattice relaxation), one has to choose in each specific case the appropriate low-frequency setup. How it may be done in practice will be seen from the experimental examples presented in the next section.

III. VARIOUS KINDS OF ELSE

As already noted, each type of longitudinal relaxation gives rise to the corresponding susceptibility; therefore, we have now to consider various kinds of longitudinal relaxation in paramagnetic solids.

In the absence of the high-frequency saturating field they are three:

1. Longitudinal spin-spin relaxation in low magnetic fields ($H_0 \lesssim H_L$);
2. Spin-spin cross relaxation;
3. Spin-lattice relaxation.

Besides, under conditions of rf saturation an additional relaxation mechanism arises, which is related to the thermal mixing in the rotating frame. Below we shall show the distinctive features of ELSE in all these cases and also how to produce and to observe it in some typical situations.

A. Susceptibility Related to the Longitudinal Spin-Spin Relaxation in Low Fields

The longitudinal spin-spin relaxation in solids is due to the nonsecular part of the spin-spin interaction Hamiltonian, namely to the terms proportional to $S_i^+ S_j^-$ and $S_i^- S_j^+$ operators (27). An elementary act of such a process consists of a "flip" of a spin S_i (or of simultaneous flips of two spins S_i, S_j in the same direction) accompanied by transfer of its (their) Zeeman energy to the spin-spin reservoir. As a result, a common spin temperature is to be established in the whole spin system, i.e., the thermal mixing of the Zeeman subsystem and the spin-spin reservoir occurs.

The probability of this process is high enough only in low magnetic fields $H_0 \lesssim H_L$, where the spectra of both subsystems are within the same frequency range. In this case the corresponding longitudinal relaxation time τ_S is of the order of the transverse relaxation time τ_2 , that is, about 10^{-6} - 10^{-8} s in dilute electronic paramagnets and 10^{-3} - 10^{-5} s in nuclear spin systems.

The associated susceptibility, subsequently denoted $\chi_S(\Omega)$, is frequently called the adiabatic susceptibility (22, 27). It should be noted, however, that this term is justified only in the frequency range $\tau_{SL}^{-1} \ll \Omega \ll \tau_S^{-1}$ (τ_{SL} is the spin-lattice relaxation time), where the entropy conservation takes place during the oscillations of the

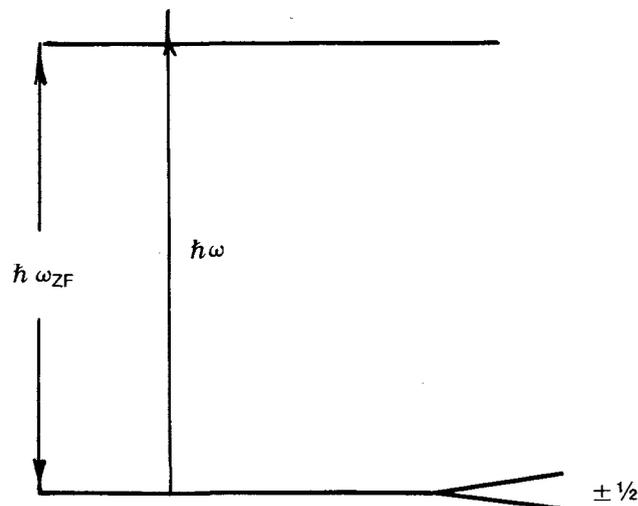


Figure 2. Energy levels of a spin system suited to observing ELSE at $H_0 = 0$.

alternating field $he^{i\Omega t}$. At higher frequencies ($\Omega \gtrsim \tau_S^{-1}$) the absorption occurs characterized by the imaginary part of $\chi_S(\Omega)$; this may be also regarded as a broad "resonance" in local fields.

If the main Hamiltonian of the spin system is purely Zeeman (particularly, at $S = 1/2$), the saturation of the "resonance" at a frequency $\omega \approx \omega_0 \approx \omega_L$ will lead only to an increase of the common spin temperature, so the susceptibility $\chi_S(\Omega)$ cannot be enhanced. Enhancement is possible, however, if the spectrum of the spin system at $H_0 = 0$ consists of at least two energy levels, the first of them being a degenerate Kramers doublet (for instance, $\pm 1/2$) and the second being separated from it by zero field splitting $\omega_{ZF} \gg \omega_L$ (see Figure 2). Such spectra are peculiar to nuclei and paramagnetic ions with $S \neq 1/2$ possessing quadrupole moments and subjected to the crystalline electric field with sufficiently low symmetry. The longitudinal spin-spin susceptibility $\chi_S(\Omega)$ is caused in this case by the Kramers doublet, while the cooling of the spin-spin reservoir can be produced by an asymmetrical saturation of the zero-field resonance at a frequency $\omega = \omega_{ZF} + \Delta$.

The experimental observation of the ELSE in such a situation has been carried out on the powder sample of paradichlorobenzene ($p\text{-C}_6\text{H}_4\text{Cl}_2$) at liquid-nitrogen temperature (17). The energy of the spin system at $H_0 = 0$ consists in this case of the quadrupole interaction of ^{35}Cl and ^{37}Cl nuclei with the electrical crystalline field gradient ($S = 3/2$, $\omega_{ZF}/2\pi \approx 35$ MHz), and of the dipole-dipole interactions of the chlorine and hydrogen nuclei ($\omega_L/2\pi \approx 10$ kHz).

The cooling of the dipole-dipole subsystem in this substance has been previously achieved by Goldman and Landesman (28), also at H_0 . However, they estimated the T_{SS} value by measuring the proton NMR immediately after a fast increase of the external magnetic field up to $H_0 \gg H_L$. Unlike this, we succeeded in observing the enhanced susceptibility $\chi_S(\Omega)$ directly at $H_0 = 0$ and $\Omega \approx \omega_L$.

The experimental data are shown in Figure 3, where the χ_S'' values measured at $\Omega/2\pi = 12$ kHz are plotted against the frequency of the rf field saturating the NQR line of ^{35}Cl nuclei. One can see that the results are in agreement with the expected behavior of the inverse spin-spin temperature β_{SS} (2-10): indeed, when the detuning is negative, the χ'' value is positive and vice versa, while at $\omega = \omega_{ZF}$ the ELSE vanishes. In the absence of the rf pumping the magnitude of χ_S'' was too small to be detected; the maximum enhancement factor $E = T_0/T_{SS}$ obtained at $\Delta/2\pi \approx 5$ kHz was estimated to be about 3.5×10^3 , in agreement with Goldman and Landesman (28).

Similar results have also been obtained on the electron spin system of the Cr^{3+} ions ($S = 3/2$) in ruby crystals ($\text{Al}_2\text{O}_3:\text{Cr}^{3+}$) at $H_0 = 0$ and liquid-helium temperatures (15). Some data are shown in Figure 4. In this case the zero-field splitting falls within the microwave band ($\omega_{ZF}/2\pi = 11.5$ GHz), while the susceptibility χ_S was measured at $\Omega/2\pi \approx 1$ MHz, that is of the order of τ_2^{-1} in this substance. The enhancement factor E is now much less than in the previous case; this is due to a rather large local field and relatively fast spin-lattice relaxation of the spin-spin reservoir (see below, Section V.C).

Note from Figures 3 and 4 that such experiments enable one to find the zero-field splitting ω_{ZF} .

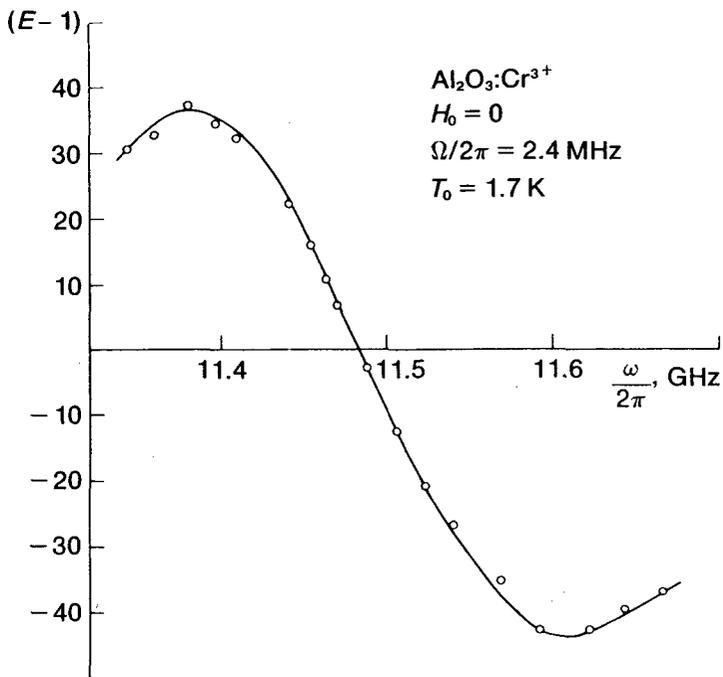


Figure 4. Enhancement factor $E = \chi_S/(\chi_S)_0$ as a function of the frequency ω of the microwave field saturating zero-field EPR of Cr^{3+} ions in ruby.

B. Cross-Relaxation Susceptibility

The spin-spin cross relaxation occurs in spin systems containing at least two spin species S_1, S_2 with similar resonance frequencies $\omega_1 \approx \omega_2$ (the so-called harmonic cross relaxation is also possible when $n\omega_1 \approx m\omega_2$, both n and m being integers) (29). In the simplest case when $S_1, S_2 = 1/2$, the cross relaxation is due to the action of the nonsecular part of the spin-spin Hamiltonian that is proportional to $S_{1i}^{\pm} S_{2j}^{\mp}$ operators. Then the elementary act of the cross relaxation consists of a flip-flop of two interacting spins S_{1i}, S_{2j} in opposite directions, the difference of their Zeeman energies being transferred to the common spin-spin reservoir and causing thereby a change of T_{SS} (3, 30, 31).

On the other hand, this process may be regarded as a thermal mixing of the spin-spin reservoir with the so-called "differential" Zeeman subsystem characterized by the Hamiltonian

$$\mathcal{H}_{\Delta} = \frac{1}{2}(c_1 S_1^z - c_2 S_2^z) \Delta_{12} \quad (8)$$

where $\Delta_{12} = \omega_1 - \omega_2$ and c_1, c_2 are the relative heat capacities of the corresponding Zeeman subsystems (9, 10, 32). From this point of view, the cross relaxation is

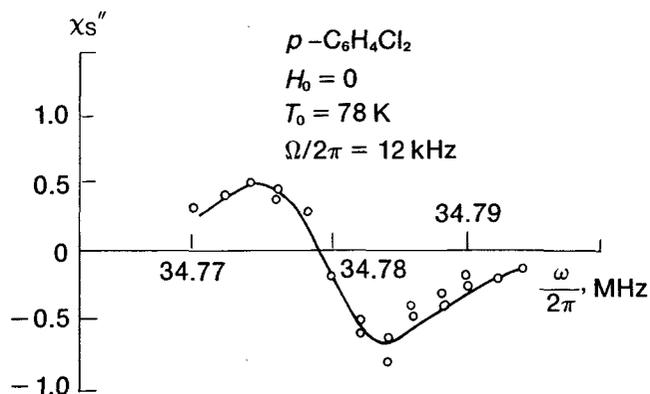


Figure 3. Enhanced susceptibility χ_S'' as a function of the frequency ω of the rf field saturating ^{35}Cl NQR in *para*-dichlorobenzene at $H_0 = 0$.

essentially similar to the longitudinal spin-spin relaxation discussed in the previous subsection, with the difference that the field H_0 is now replaced by the detuning Δ_{12} , and that the cross-relaxation time τ_{CR} exceeds as a rule the τ_2 value.

If the cross relaxation is effective in comparison with the spin-lattice relaxation, the process will tend to establish a dynamic equilibrium characterized by the relation (30, 31):

$$\omega_1\beta_{1Z} - \omega_2\beta_{2Z} = \Delta_{12}\beta_{SS} \quad (9)$$

where β_{1Z} , β_{2Z} are the inverse Zeeman temperatures of the spins S_1 , S_2 , respectively (this relation expresses the equality between T_{SS} and the spin temperature of the subsystem \mathcal{H}_Δ). In crystals containing nuclei or paramagnetic ions with $S > 1/2$ and characterized by multilevel nonequidistant energy spectra, the subsystems S_1 and S_2 are usually various pairs of energy levels, and the detuning Δ_{12} usually depends strongly on the external field H_0 . This means that any small increment δH_0 of the field H_0 produces in such systems a change of Δ_{12} , and so upsets the equilibrium of Eq. (9). As a result, a redistribution of the spins among the energy levels occurs, producing a change δM_z in the longitudinal magnetization and so leading to the appearance of a cross-relaxation susceptibility $\chi_{CR} = \delta M_z / \delta H_0$.

It is clear from Eq. (9) that χ_{CR} depends directly on β_{SS} ; that is confirmed by exact calculations (11) (see Section IV). Particularly, it is found that at fixed values of Δ_{12} and Ω , the χ_{CR} magnitude is proportional to β_{SS} and, consequently, can be enhanced by means of the asymmetrical saturation of any resonance line belonging to the spin system under consideration.

An experimental example of this type of ELSE is shown in Figure 5. The experiments were performed on ruby crystals with chromium concentration $c = 0.035\%$ at liquid-helium temperatures (12, 14). The conditions for cross relaxation between different transitions of the four-level EPR spectrum of Cr^{3+} were set by choosing the angle θ between H_0 and the crystallographic axis (see top of Figure 5). The imaginary part of the susceptibility χ_{CR}'' was measured at frequencies $\Omega/2\pi$ in the range 10^5 - 10^6 Hz with the aid of the ordinary autodyne NMR spectrometer.

Using a customary procedure of magnetic spectroscopy, the χ_{CR}'' value was measured as a function of H_0 at $\Omega = \text{const}$. The signal was registered using deep 50-Hz modulation of the magnetic field about the value H_0^{CR} corresponding to zero detuning ($\omega_1 = \omega_2$) and has a maximum at this point (Figure 5). As will be shown in Section IV, such a dependence of χ_{CR}'' on Δ_{12} agrees well with the theory if $\Omega \gg \tau^{-1}$ (11, 14).

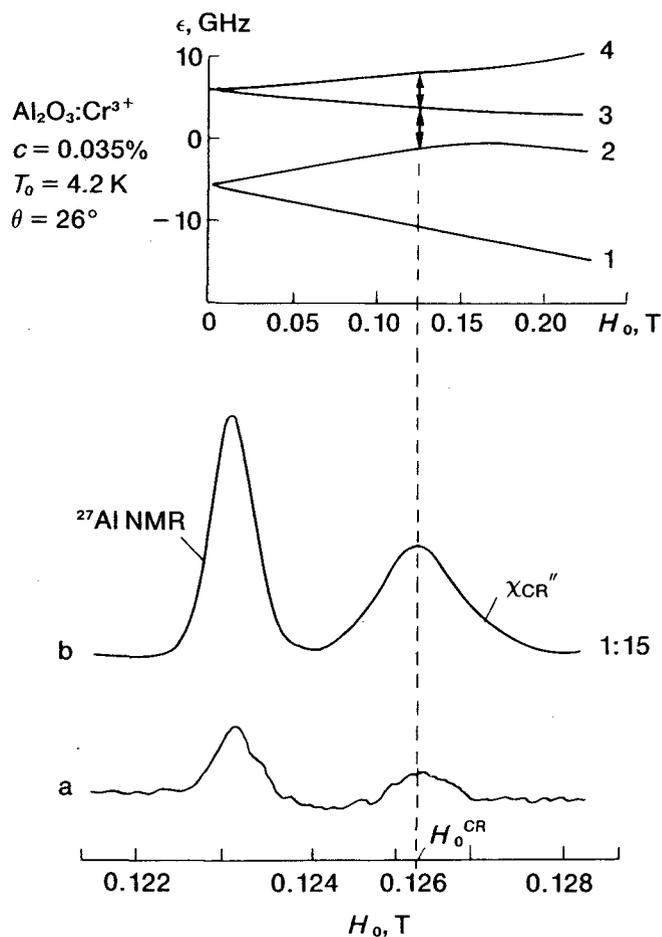


Figure 5. Top: energy-level diagram of Cr^{3+} ion in ruby under conditions of cross relaxation (the involved transitions are indicated by arrows).

Bottom: the oscillograms of χ_{CR}'' and ^{27}Al NMR signals at equilibrium (a) and under conditions of the off-center microwave saturation of the $2 \rightarrow 3$ transition in the EPR spectrum (b).

The cooling of the spin-spin reservoir was accomplished by saturating the wing of an EPR line (in the case shown in Figure 5, the low-frequency wing of the line corresponding to the $2 \rightarrow 3$ transition was saturated at a wavelength of 3.2 cm, the energy levels being numbered upwards). As seen from the figure, it leads to a sharp increase of the susceptibility ($E = T_0/T_{SS} = +40$). When the opposite wing of the EPR line was saturated, the inversion of the absorption signal (the stimulated emission) took place, but the gain had the same absolute value.

By suitable choice of the frequency Ω , the NMR spectrum of ^{27}Al nuclei belonging to the host lattice could be observed simultaneously with the χ_{CR}'' signal. (To this

end, the axis of the pick-up coil was inclined somewhat to the H_0 direction). The NMR line is also shown in Figure 5; it is seen that the enhancement factors of χ_{CR}'' and NMR signals are exactly equal to each other. Since the χ_{CR}'' value is proportional to β_{SS} , this result seems to be the most direct experimental proof of the existence of a strong coupling between the nuclear Zeeman subsystem and the electron spin-spin reservoir (6, 7). This will be considered in more detail in Section V.

C. Longitudinal Susceptibility in the Rotating Frame

As noted in Section II, under conditions of saturation of the magnetic resonance, it is convenient to transfer into the rotating reference frame, where the spin system is acted upon by a static effective magnetic field (26):

$$H_e = \sqrt{H_1^2 + (\Delta/\gamma)^2}$$

making an angle

$$\theta = -\tan^{-1}(\gamma H_1/\Delta)$$

with the z -axis. At $H_e \lesssim H_L$ the Zeeman energy of the spins in the effective field H_e mixes with that of the spin-spin interaction, giving rise to the longitudinal (relative to \vec{H}_e) relaxation with a characteristic time τ_S^* (10).

If $H_1 \ll H_L$ (Provotorov's case), one can assume that \vec{H}_e is parallel to z , and the relaxation time is given by (2):

$$(\tau_S^*)^{-1} = 2W(\Delta)(1 + \frac{\Delta^2}{\omega_L^2}) \quad (10)$$

where $W(\Delta)$ is the probability of the transitions induced by the field $2H_1 \cos \omega t$. Then the associated susceptibility χ_S^* (Ω) is analogous to that described for the case of a low external field. However, χ_S^* exists only in the presence of the saturating field and depends strongly on its magnitude H_1 .

This kind of ELSE was experimentally observed in the nuclear spin system of ^{19}F nuclei in CaF_2 crystals at $T_0 = 4.2$ K and $H_0 = 0.35$ T (13). The sample was placed in a system of two crossed coils, one of which was used to saturate the NMR at a frequency $\omega/2\pi = 14$ MHz, and the other, with its axis parallel to H_0 , was used to register χ_S^* at a frequency $\Omega/2\pi = 1.16$ kHz (the low-frequency coil had up to 6000 turns). The oscillograms of the absorption and dispersion signals, which are proportional to $(\chi_S^*)''$ and $(\chi_S^*)'$, respectively, are shown in Figure 6 (in this case $H_1 = 0.056$ mT, $H_L = 0.088$ mT). They were obtained with isentropic passage of the field H_0 through the NMR line under saturation conditions. As

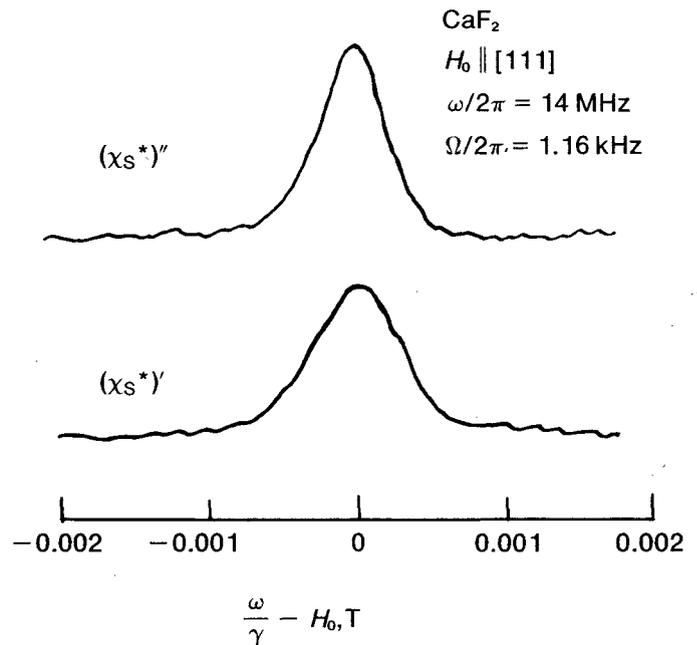


Figure 6. Signals of the absorption (upper trace) and dispersion (lower trace) due to the susceptibility χ_S^* , obtained with isentropic passage of the ^{19}F NMR line on CaF_2 crystal at 4.2 K. The sweep time is 1 s.

is well known (33), for such a passage the sign of T_{SS} does not change, and the maximum of $|\beta_{SS}|$ is reached at $\Delta = 0$ (i.e., at the center of the line). This agrees with the signal shapes in Figure 6.

Since $\chi''/\chi' = \Omega\tau$, (see Eqs. (3), (4)), from such signals it is easy to determine the characteristic time τ_S^* as a function of Δ and H_1 (18, 19).

After successive passages, the signals of the type shown in Figure 6 decrease gradually to zero, thus indicating that T_{SS} increases because of spin-lattice relaxation in the rotating frame and because of deviation from ideal entropy conservation due to so-called "saturation by modulation" (34). It is clear that such experiments enable one to get information on these phenomena.

The ELSE of the same type was also observed on the electron spin system of Cr^{3+} ions in ruby (35). In this work the χ_S^* signal was detected under steady-state conditions, while the cooling of the spin-spin reservoir was ensured by the nonresonant cross relaxation between two other (not saturated) transitions of the EPR spectrum. A pronounced distinction appears between χ_S^* and χ_{CR} signals in that the former disappears just at the instant when the microwave pumping is switched off, while the latter decreases gradually towards its equilibrium value with a characteristic relaxation time (see Section V.B).

If the condition $H_1 \ll H_L$ is not fulfilled, one cannot consider \vec{H}_e to be parallel to the z -axis. In this case a low-frequency coil oriented along \vec{H}_0 will detect signals proportional to

$$(\chi_{S^*})_{zz} = \chi_{ZZ} \cos^2 \theta + \chi_{XX} \sin^2 \theta \quad (11)$$

where χ_{ZZ} and χ_{XX} are respectively, the longitudinal and transverse susceptibilities in a new rotating frame, TRF, which is tilted to the z -axis at an angle θ (26) (see Figure 7). Finally, when H_1 becomes much larger than H_L , the dependence of χ_{XX} on Ω takes the form of a resonance line having its maximum at $\Omega = \gamma H_e$. This phenomenon, which is nothing but magnetic resonance in the tilted rotating frame, was experimentally observed on ^{19}F nuclei in some crystals (18, 19); it will be described in a little more detail in Section V.E. Note that, as long as $H_e \gg H_L$, a common spin temperature cannot be established in the TRF, and hence the χ_{XX} is not proportional to β_{SS} . So, strictly speaking, the low-frequency resonance in the TRF is beyond the field of ELSE proper, though both phenomena are quite similar from the operational point of view.

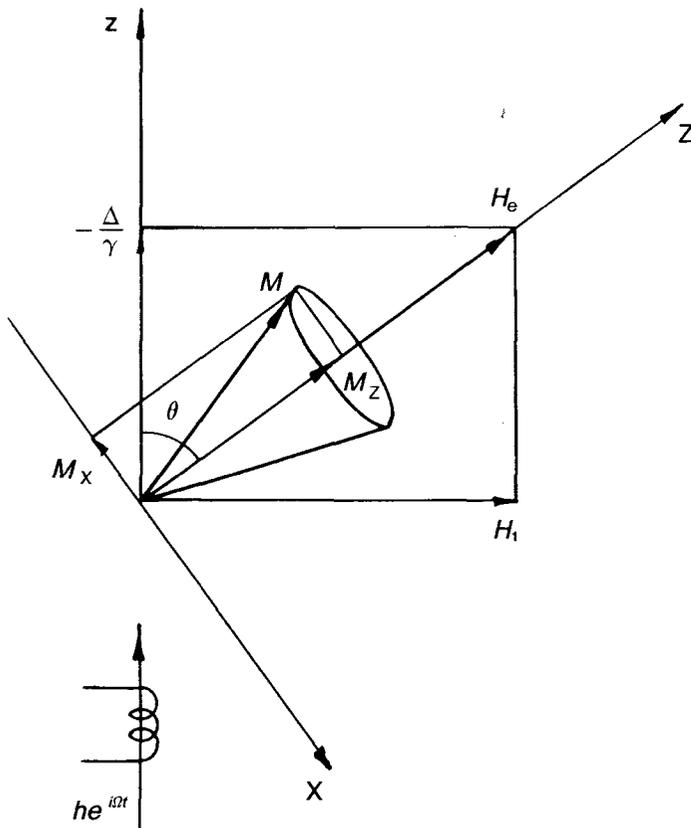


Figure 7. Vector diagram of magnetic fields and magnetizations in the rotating frame.

D. Susceptibility Related to the Spin-Lattice Relaxation

In the absence of a saturating field the susceptibility $\chi_{SL}(\Omega)$, related to the spin-lattice relaxation, is described by an expression of the type of Eq. (2) with $\tau = \tau_{SL}$, i.e., it reaches its maximum at $\Omega \leq \tau_{SL}^{-1}$.

However, under saturation conditions and, consequently, in the rotating frame, the relaxation time τ_{SL}^* is not equal to τ_{SL} , and at $H_1 \ll H_L$ it is given by the expression:

$$(\tau_{SL}^*)^{-1} = \frac{\tau_{SL}^{-1} \Delta^2 + \tau_{SSL}^{-1} \omega_L^2}{\Delta^2 + \omega_L^2} \quad (12)$$

where τ_{SSL} is the time of spin-lattice relaxation of the spin-spin reservoir (12). Although as a rule $\tau_{SL}^* < \tau_{SL}$, this relaxation process remains rather slow, so ELSE may be registered only at very low frequencies (in the range 10^2 - 10^5 Hz for EPR and less than 100 Hz for NMR). Nevertheless, such experiments seem to be feasible, at least in the former case, although they have not yet been realized.

IV. THEORY

The above discussion enables one to get only qualitative estimates of the magnitude of ELSE. The more rigorous theory, which is essential for quantitative comparison with experimental data, has been developed by Atsarkin (11), as well as by Buishvili et al (36-38) and Shaposhnikov and Kadyrov (39). It is not necessary here to describe these calculations in detail, so we will restrict ourselves to a brief outline of the principal ideas and the most important results.

A. Description Based on Provotorov's Equations

We return to the simplest spin system consisting of N identical spins of $S = 1/2$ in a large external field $H_0 \gg H_L$, and suppose that the resonance line at frequency $\omega_0 = \gamma H_0$ is homogeneously broadened by spin-spin interactions. In the high-temperature approximation ($\hbar \omega_0 \ll kT_0$), the saturation of such a system with an rf field $2H_1 \cos \omega t$ ($H_1 \ll H_L$, $\omega \approx \omega_0$) can be described by Provotorov's equations for Zeeman and spin-spin inverse temperatures β_Z and β_{SS} , respectively (2):

$$\left. \begin{aligned} \frac{d}{dt}(\omega_0 \beta_Z) &= -2W(\Delta)(\omega_0 \beta_Z + \Delta \beta_{SS}) - \tau_{SL}^{-1}(\omega_0 \beta_Z - \omega_0 \beta_0) \\ \frac{d}{dt}(\beta_{SS}) &= -\frac{2\Delta}{\omega_L^2} W(\Delta)(\omega_0 \beta_Z + \Delta \beta_{SS}) - \tau_{SSL}^{-1}(\beta_{SS} - \beta_0) \end{aligned} \right\} (13)$$

where

$$W(\Delta) = \frac{\pi}{2} (\gamma H_1)^2 g(\Delta) \quad (14)$$

and $g(\Delta)$ is the absorption line shape normalized to unit area. When measuring the longitudinal susceptibility $\chi(\Omega)$ at frequency $\Omega \ll \omega_0$, the sample is, in addition, subjected to a weak alternating field $he^{i\Omega t}$ parallel to H_0 , which leads to the oscillations of the detuning Δ at the frequency Ω . Thus one has to solve Provotorov's equations under conditions of low-frequency longitudinal modulation.

This problem was previously considered by several authors, for example, Goldman (10,34). However, their aim was in essence the opposite of ours, since they calculated the influence of the modulation on the resonance signals detected at a frequency ω , whereas we seek to determine the influence of the resonance saturation on the signals $\chi'(\Omega)$ and $\chi''(\Omega)$, which are detected in the modulation circuit itself.

An illustrative example of such calculations is the evaluation of the susceptibility, χ_{S^*} , associated with thermal mixing in the rotating frame. In this case a strong saturation is assumed [$W(\Delta) \gg \tau_{SL}^{-1}, \tau_{SSL}^{-1}$], and only the frequency range $\Omega \gg \tau_{SL}^{-1}, \tau_{SSL}^{-1}$ is considered, so the spin-lattice relaxation can be neglected. As a result, the system (13), in which it is now necessary to omit the lattice terms, reduces to the equation of the type of Eq. (1) describing the longitudinal relaxation of the magnetization M_z towards some "adiabatic" value M_z^{ad} . The corresponding relaxation time τ_{S^*} is given by Eq. (10); it characterizes the rate of the thermal mixing in the rotating frame (2).

Then, by analogy with Eqs. (1) and (2), one gets immediately:

$$\chi_{S^*}(\Omega) = \frac{(\chi_{S^*})_{ad}}{1 + i\Omega\tau_{S^*}} \quad (15)$$

where $(\chi_{S^*})_{ad} = \partial M_z^{ad} / \partial H_z$ is the value of χ_{S^*} being measured at sufficiently low frequencies $\Omega \ll 1/\tau_{S^*}$. With such a slow modulation, the saturation is completed "at each instant," so the change of Δ is a thermodynamically adiabatic process, and entropy conservation takes place (5):

$$\omega_L^2 \beta_{SS}^2 + \Delta^2 (\beta_Z^*)^2 = \text{const}, \quad (16)$$

where

$$\beta_Z^* = -\frac{\omega_0}{\Delta} \beta_Z$$

is the inverse Zeeman temperature in the rotating frame. By taking the equality $\beta_Z^* = \beta_{SS}$ into account (it is caused by the thermal mixing in the rotating frame), one gets from Eq. (16):

$$(\chi_{S^*})_{ad} = \chi_0 \cdot \frac{\beta_{SS}}{\beta_0} \cdot \frac{\omega_L^2}{\Delta^2 + \omega_L^2}, \quad (17)$$

where

$$\chi_0 = \frac{\gamma^2 \hbar^2 N \beta_0}{4k}$$

and the β_{SS} value is determined by the state of the system at the instant the susceptibility is measured. In particular, immediately after completion of saturation but before the influence of the lattice comes into play, with initial conditions $\beta_Z(0) = \beta_{SS}(0) = \beta_0$, one gets from Eqs. (13):

$$\beta_{SS} = -\beta_0 \cdot \frac{\omega_0 \Delta}{\Delta^2 + \omega_L^2}, \quad (18)$$

whereas in steady state

$$\beta_{SS} = -\beta_0 \cdot \frac{\omega_0 \Delta}{\Delta^2 + a\omega_L^2} \quad (19)$$

where $a = \tau_{SL}/\tau_{SSL}$ (see, for example, ref. (2-6)).

Thus, as expected, the χ_{S^*} value is proportional to β_{SS} and exceeds χ_0 by a factor of about ω_0/ω_L .

The above derivation was performed on the assumption that the amplitude h of the longitudinal alternating field is small enough to prevent so-called "saturation by modulation" (34), i.e., an increase of T_{SS} due to the absorption of low-frequency energy. Manifestations of this effect in ELSE experiments will be described in Section V.B.

A similar approach may be used in calculating the cross-relaxation susceptibility $\chi_{CR}(\Omega)$. If the cross relaxation is much more effective than the spin-lattice relaxation, it leads to thermal mixing of the spin-spin reservoir with the "differential" subsystem characterized by the Hamiltonian of Eq. (8) and by the inverse spin temperature (9, 10):

$$\beta_\Delta = \frac{\omega_1 \beta_{1Z} - \omega_2 \beta_{2Z}}{\Delta_{12}} \quad (20)$$

The characteristic time of this mixing is (30):

$$\tau_{CR}^{-1} = W_{CR}(\Delta_{12}) \left(1 + \frac{b \Delta_{12}^2}{\omega_L^2}\right) \quad (21)$$

where $W_{CR}(\Delta_{12})$ is the probability of the cross relaxation with a detuning $\Delta_{12} = \omega_1 - \omega_2$, $b = N_1 N_2 / (N_1 + N_2)^2$, and N_1 and N_2 are the numbers of the spins S_1 and S_2 , respectively (it is assumed that S_1 and S_2 are both 1/2). Then the cross-relaxation susceptibility is given by

$$\chi_{CR}(\Omega) = \frac{\chi_{CR}^{ad}}{1 + i\Omega\tau_{CR}} \quad (22)$$

where

$$\chi_{CR}^{ad} = \beta_{SS} \frac{\hbar^2 (N_1 + N_2) (\gamma_1 - \gamma_2)^2}{4k} \cdot \frac{b\omega_L^2}{\omega_L^2 + b\Delta_{12}^2} \quad (23)$$

The spectroscopic splitting factors γ_1, γ_2 must be taken here in the differential sense, i.e., as $d\omega/dH_0$. This is essential if the energy of the spins is not purely Zeeman, for example, when the cross relaxation occurs in a multilevel nonequidistant spin system (see Figure 5). In this case, which is the most important case in practice, Eq. (23) may be generalized using the rate equations obtained by Rodak (40).

It is clear that Eqs. (22) and (23) are valid irrespective of the action of the saturating field (provided $W(\Delta) \ll W_{CR}(\Delta_{12})$), whereas the β_{SS} value in Eq. (23) depends strongly on saturation. Particularly, when the spin-spin reservoir is cooled by saturating the wing of a resonance line, β_{SS} is determined by expressions of the type of Eqs. (18) and (19), while at equilibrium with the lattice $\beta_{SS} = \beta_0$.

From Eqs. (21) to (23) one can derive the expression for the imaginary part of the susceptibility $\chi_{CR}''(\Omega)$ measured at relatively high frequencies $\Omega \gg \tau_{CR}^{-1}$:

$$\chi_{CR}''(\Omega) = \beta_{SS} \frac{\hbar^2(\gamma_1 - \gamma_2)^2 N_1 N_2}{4k(N_1 + N_2)} \cdot \frac{W_{CR}(\Delta_{12})}{\Omega} \quad (24)$$

This relation may be useful in determining the function $W_{CR}(\Delta_{12})$ (see Section V.D).

Using Provotorov's equations, it is also possible to find the susceptibility χ_{SL}^* related to spin-lattice relaxation in the rotating frame (11).

As to the susceptibility, χ_S , associated with the spin-spin relaxation at low fields, the corresponding calculation would be more complicated because of degeneration of the Kramers doublet. Nevertheless, the proportionality between χ_S and β_{SS} also holds in this case.

B. Other Approaches

Provotorov's equations are applicable only within time intervals $t \gg \tau_2$, where the quasi-equilibrium characterized by spin temperatures T_Z and T_{SS} has enough time to be established. This means that at relatively high frequencies $\Omega \gg 1/\tau_2$, the above consideration does not apply and another approach has to be developed.

This problem was tackled by Buishvili et al (36). They used the fluctuation-dissipation theorem that relates the imaginary part of the susceptibility $\chi''(\Omega)$ to the Fourier transform of the correlation function of the operator $M_z(t)$. By calculating this correlator from the quantum master equation, the following expression was obtained for the susceptibility $\chi_S^*(\Omega)$ at frequencies $\Omega \gg W(\Delta)$:

$$(\chi_S^*)''(\Omega) = \chi_0 \frac{\beta_{SS}}{\beta_0} \cdot \frac{W(\Delta + \Omega) + W(\Delta - \Omega)}{2\Omega} \quad (25)$$

If Ω is higher than $W(\Delta)$ but lower than the resonance line width $\Delta\omega$, Eq. (25) coincides with Eqs. (15) and (17). At still higher frequencies, however, the $(\chi_S^*)''$ value begins to decrease faster than as $1/\Omega$, and finally at $\Omega \gg \Delta, \Delta\omega$, it becomes proportional to $g(\Omega)/\Omega$. Besides, as seen from Eq. (25), at $\Delta = \pm\Omega$ two peaks of absorption arise, which may be understood as a resonance in the effective field $H_e = -\Delta/\gamma$ acting in the rotating frame. A similar generalization was also performed for the cross-relaxation susceptibility $\chi_{CR}(\Omega)$ (36). An extension of the theory to inhomogeneously broadened resonance lines, both for fast spectral diffusion and for isolated spin packets, including the case $H_1 > H_L$, has also been developed (37, 38).

An essentially different approach to the theoretical description of ELSE was developed by Shaposhnikov and Kadyrov (39). In this paper the enhanced longitudinal susceptibility (χ_S^* in our notation) is deduced from the phenomenological master equations for the macroscopic magnetization that were previously evaluated by the same authors (41). Note that in ref. (39) the influence of the longitudinal spin-spin relaxation in the laboratory frame, i.e., the contribution of χ_S , was simultaneously taken into account.

V. APPLICATIONS OF ELSE

A. General Remarks

The most obvious sphere of application of ELSE is a considerable improvement of the sensitivity of the old "parallel-field" method, which now becomes comparable with the magnetic-resonance sensitivity.

Another application is the possibility of the detection of magnetic- and quadrupole-resonance spectra by using some sort of double resonance, where the spin system is saturated at a high frequency $\omega \approx \omega_0$, while the signal is monitored at a low frequency Ω by means of the ELSE technique. This enables one to record spectra without any high-frequency receiver; it is particularly convenient in searching for zero-field splittings at $H_0 = 0$ (see Section III.A, Figures 3 and 4).

Furthermore, the measurement of χ_S^* at $H_1 \lesssim H_L$ yields information on relaxation and thermal mixing in the rotating frame, while at $H_1 \gg H_L$ a new way for improving the NMR resolution in solids may be suggested by the use of the resonance in the effective field.

The last and perhaps the most important field of application of ELSE is as a thermometer for measuring the temperature of the spin-spin reservoir, noting that in all cases the enhanced susceptibility is proportional to T_{SS}^{-1} . This is of particular value for EPR, where the only method of measuring T_{SS} so far has been to observe the

antisymmetrical component in the EPR absorption line. Furthermore, this component, which is itself quite weak, must be observed against the background of a strong symmetrical signal due to the Zeeman subsystem (42-44).

In the following sections it will be shown how some of these possibilities are realized in studies of spin dynamics and relaxation.

B. Thermal Contact Between the Nuclear Zeeman System and the Electron Spin-Spin Interaction Reservoir

In solids containing both nuclear spins I of the host lattice and electron spins S of paramagnetic impurity, there can exist a strong coupling between the electron spin-spin interaction reservoir (ESSR) and the nuclear Zeeman subsystem (NZS), and this coupling leads to equalization of their temperatures T_{SS} and T_{IZ} . This phenomenon (the so-called direct thermal contact between the ESSR and the NZS) was theoretically predicted in 1964-65 (45, 46) and was soon observed experimentally in ruby crystals (47), and then in other objects (see, for example, the reviews (6-9)). At low temperatures the direct thermal contact with ESSR frequently ensures the most effective coupling channel between the NZS and the lattice, and can therefore play a decisive role in such important phenomena as the dynamic polarization and the spin-lattice relaxation of nuclei, ENDOR, and others.

In the above papers, however, only the existence of the thermal contact between ESSR and NZS could essentially be established, while practically nothing was known concerning the kinetics and the rate of the establishment of equilibrium between the two subsystems

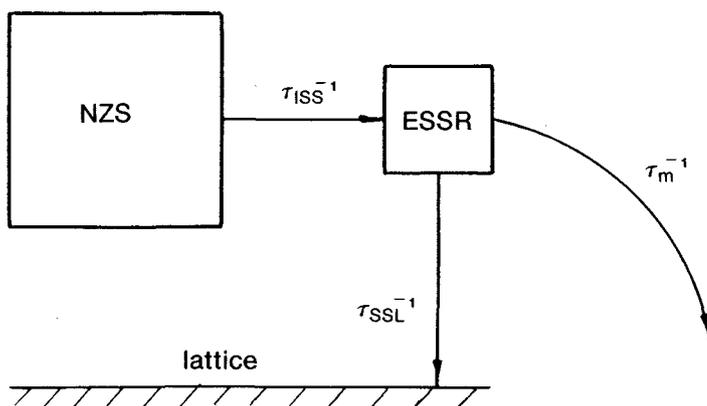


Figure 8. Connections between the nuclear Zeeman subsystem (NZS), the electron spin-spin reservoir (ESSR), and the lattice. Arrows indicate relaxations. τ_m^{-1} is the rate of additional heating due to low-frequency modulation.

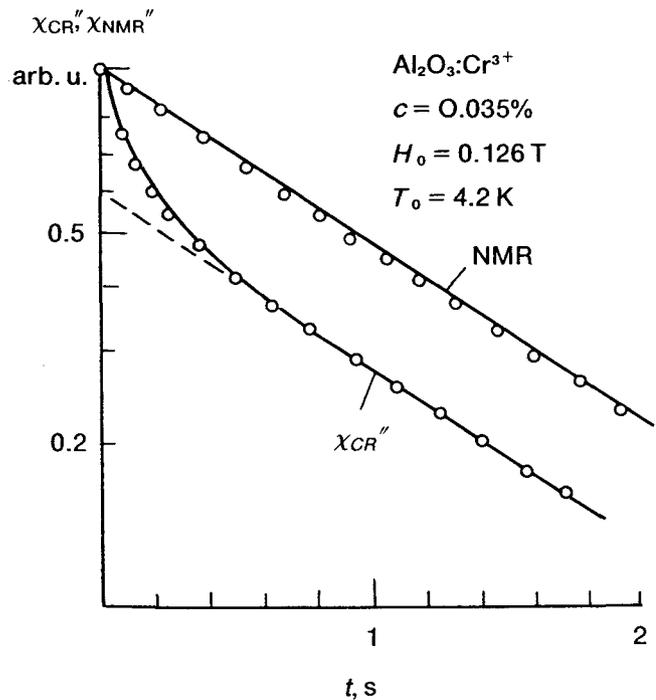


Figure 9. Decays of the enhanced susceptibility signal χ_{CR}'' (lower curve) and of the ^{27}Al NMR signal (upper curve) in ruby after switching off the microwave pumping.

(note that references (48-50) give recently acquired information on this subject).

Application of ELSE to this problem implies the following procedure (16). First, both NZS and ESSR must be strongly cooled by the appropriate off-center saturation of the EPR. Then the microwave pumping has to be switched off, and the free spin-lattice relaxation of both subsystems occurs. In the course of this process, the spin temperatures $T_{SS}(t)$ and $T_{IZ}(t)$ are measured by simultaneously recording both the NMR signal of the lattice nuclei and the enhanced longitudinal susceptibility (for instance, χ_{CR}'' , just as in Figure 5).

The relations between ESSR, NZS, and the lattice are shown in Figure 8 (the direct NZS-lattice relaxation is neglected). According to this figure, the relaxation of both inverse spin temperatures, β_{SS} and $\beta_{IZ} \equiv T_{IZ}^{-1}$, consists of two exponentials, "fast" and "slow," with amplitudes A_f , A_{sl} and with respective times τ_f and τ_{sl} (46). In principle, by measuring these parameters, the characteristic time of the coupling between NZS and ESSR (τ_{ISS}), the spin-lattice relaxation time of ESSR (τ_{SSL}), as well as the ratio of thermal capacities of both subsystems, $K = c_{IZ}/c_{SS}$, can be determined.

The experiments were performed on ruby in the range of Cr^{3+} concentrations $c = 0.02\% - 0.06\%$, at temperatures 2.0-4.2 K, for orientations of H_0 that ensured the effective cross relaxation in the EPR spectrum (16).

A typical result is shown in Figure 9. The decay of the polarization of ^{27}Al nuclei is singly exponential, whereas the decay of χ_{CR} is doubly exponential, in agreement with theoretical predictions for the case $K \gg 1$ (16, 46). From these curves the quantities of interest (τ_{ISS} , τ_{SSL}) can be easily found.

However, in some cases the less favorable situation takes place. Indeed, if the bottleneck of the relaxation process is situated on the ESSR-lattice section (see Figure 8), both subsystems relax with a single (slow) exponential and hence the determination of τ_{ISS} becomes impossible. Fortunately, this difficulty can be got around with the same ELSE technique, merely by increasing the amplitude h of the low-frequency magnetic field used for measuring χ_{CR} . In fact, this field is partly absorbed by the spin system (χ_{CR} is just the absorption coefficient), causing an additional heating of the ESSR, i.e., "saturation by modulation" (34). As long as the heating rate τ_m^{-1} (proportional to h^2) is small in comparison with τ_{SSL}^{-1} , this effect may be neglected; but if h is increased sufficiently, it is always possible to ensure fulfillment of the condition $\tau_m \ll \tau_{\text{SSL}}$, i.e., to "short-circuit" the spin-lattice relaxation of the ESSR and shift the bottleneck to the NZS-ESSR section (Figure 8).

This effect is shown in Figure 10. It is seen that on increase of h , the nuclear spin-lattice relaxation time $\tau_{\text{IL}} = \tau_{\text{sl}}$ initially decreases and then tends asymptotically to a constant value, which is identified with τ_{ISS} . Thus, the ELSE method enables one to determine directly the

Table 1. Characteristic times τ_{ISS} of the Coupling Between the Zeeman Subsystem of ^{27}Al Nuclei and the Spin-Spin Reservoir of Cr^{3+} Ions in Ruby at $T_0 = 1.7\text{-}4.2\text{ K}$.

Cr^{3+} concentration, %	0.018		0.035		0.055	
H_0, T	0.125	0.450	0.125	0.450	0.125	0.450
$\tau_{\text{ISS}}, \text{s}$	2.0	7.0	0.45	1.0	0.18	0.45

NZS-ESSR coupling rate in a range of H_0 , T_0 , and c . These data are presented in Table 1. The τ_{ISS} values were found to be independent of temperature in the range 2.0-4.2 K. These data are interpreted (16) on the basis of the spin-diffusion theory (51).

An unexpected result was obtained for τ_{SSL} , which was found to be considerably larger than the well-known Zeeman spin-lattice relaxation time in ruby, $\tau_{\text{SL}} \sim 0.2\text{-}0.4\text{ s}$; this result seems quite unrealistic. Besides, the K values obtained in the same experiments did not agree with reasonable estimates. To explain these contradictions, it was proposed (16) that an appreciable fraction (up to 20%) of the ^{27}Al spins are coupled to the ESSR more strongly than to the remaining nuclei. This leads to an apparent increase of the heat capacity of the ESSR and to slowing down of its relaxation.

Although such a modified model gives better agreement with theory, all difficulties have not been resolved. These could probably be resolved only if the spatial inhomogeneity of the nuclear polarization were

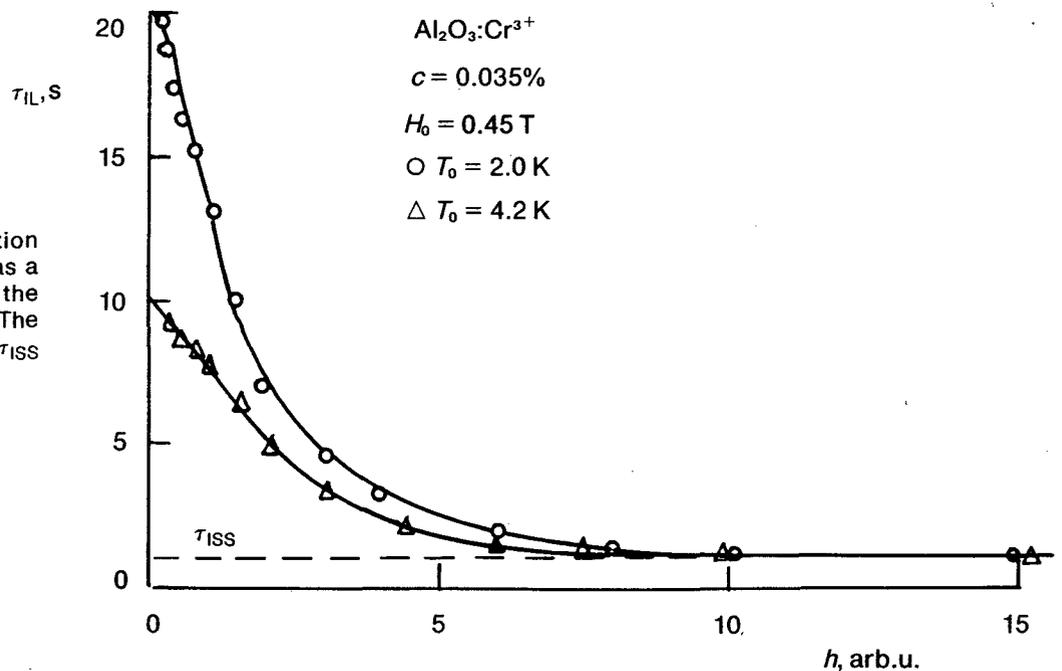


Figure 10. Spin-lattice relaxation time τ_{IL} of ^{27}Al nuclei in ruby as a function of the amplitude h of the alternating low-frequency field. The broken line represents the τ_{ISS} value.

properly taken into account. This, in turn, calls for further development of the theory of the nuclear spin diffusion. One can hope that the procedure described here, which makes it possible to follow the behavior of the nuclear spins "from the inside" (i.e., from the side of the ESSR and of the neighboring nuclei), will be useful in solving this problem.

C. Spin-Lattice Relaxation of the Electron Spin-Spin Reservoir

Although the electron spin-lattice relaxation in paramagnetic solids has been extensively studied for many years, practically no information is yet available on the relaxation rate of the electron spin-spin reservoir, in contrast to the well-explored spin-lattice relaxation of the nuclear dipole-dipole reservoir (10). Some estimates concerning τ_{SSL} may be obtained from the experiments described in the previous section. However, as noted above, the interpretation of these data is difficult because of the strong coupling between the ESSR and the lattice nuclei.

To overcome this difficulty and to measure directly the true τ_{SSL} value, another set of ELSE experiments has been carried out, also on ruby crystals but now at $H_0 = 0$ (20). In this case the energy of ^{27}Al nuclear spins comprises only their relatively small quadrupole splitting, so

the corresponding heat capacity is much less than c_{SS} (at least at $c \lesssim 0.03\%$), and cannot appreciably affect the spin-lattice relaxation of the ESSR.

The enhancement of the "spin-spin" susceptibility χ_S was produced in these experiments as described in Section III.A (see Figure 4), while the τ_{SSL} value was directly measured from the decay of the signal $\chi_S(t) \propto \beta_{SS}(t)$ after switching off the microwave pumping. Some experimental data obtained at $T_0 = 1.7$ K are shown in Figure 11, where the τ_{SL} values (52) are also given for comparison.

It is seen that τ_{SSL} depends strongly on Cr^{3+} concentration. One can also see that, in spite of a considerable scatter in the data, in most cases the ratio $a = \tau_{SL}/\tau_{SSL}$ falls within the range from 2 to 6. On the other hand, the calculations performed by us for this case ($H_0 = 0$) assuming various kinds of spin-spin interactions (dipole-dipole, exchange, hyperfine, etc.) lead to $0.5 \leq a \leq 1.0$ (unlike the case of the dipole-dipole interaction at $H_0 \gg H_L$ where $a = 3$ (10)). This discrepancy between theory and experiment may be attributed to the influence of some foreign fast-relaxing impurities (Cr^{2+} , Fe^{2+} , etc. (53, 54)), as well as of the Cr^{3+} exchange-coupled pairs and triads (55, 56).

Information on this subject can be obtained from the temperature dependence of τ_{SSL} (Figure 12). As seen from the figure, the experimental data may be fitted to the expression:

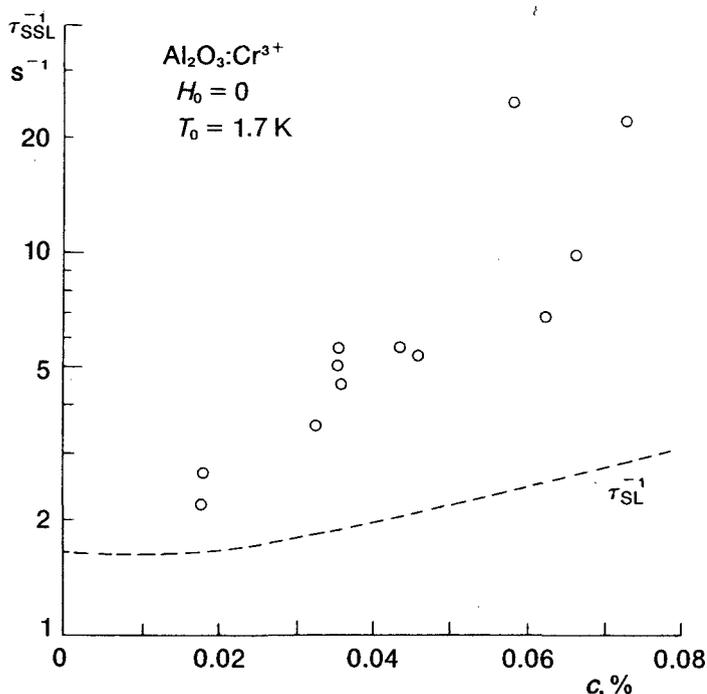


Figure 11. Spin-lattice relaxation rate of the electron spin-spin reservoir in ruby (τ_{SSL}^{-1} , open circles) as a function of Cr^{3+} concentration (c). The broken curve represents the "usual" spin-lattice relaxation rate τ_{SL}^{-1} , (52).

$$\tau_{SSL}^{-1} = AT_0 + B \exp(-\Delta E/kT_0) \quad (26)$$

where $\Delta E/k = 18.5$ K, while the B value changes significantly from sample to sample. One can suggest that the energy E is related to a characteristic splitting in the

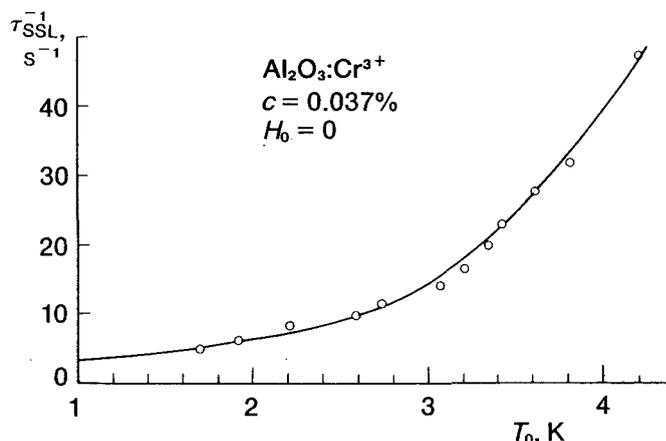
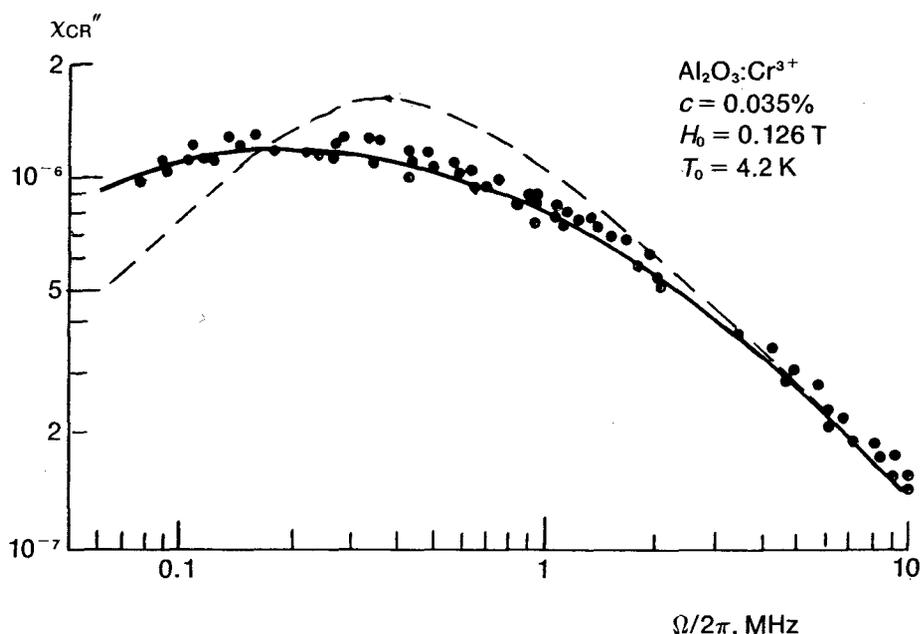


Figure 12. Spin-lattice relaxation rate of the ESSR in ruby versus the lattice temperature. The solid curve is calculated according to Eq. (26) with $A = 3\text{s}^{-1}/\text{K}$; $B = 2.9 \times 10^3\text{s}$; $E/k = 18.5$ K

Figure 13. The absorption part of cross-relaxation susceptibility (χ_{CR}'' , black points) versus the frequency Ω under conditions of resonant cross relaxation in ruby. The broken curve corresponds to Eq. (22); the solid curve is calculated by taking into account the spatial distribution of τ_{CR} values.



spectrum of fast-relaxing clusters; in particular, a suitable splitting is found in the spectrum of the third-next-neighbor exchange pair of Cr^{3+} ions separated by 3.18 Å (57). If this interpretation is true, one will be able to regard the B value as a measure of the pair concentration and in this way to get information on spatial distribution of paramagnetic ions.

D. Cross Relaxation

Measuring the “ordinary” (not enhanced) low-frequency longitudinal susceptibility $\chi_{CR}(\Omega)$ is the earliest method of studying the electron-spin cross relaxation (note that cross relaxation itself had been discovered by this method (58)). ELSE sharply improves the sensitivity of such measurements, allowing experiments on strongly diluted paramagnets. One of the advantages of this method is the possibility of taking measurements at small detuning Δ_{12} (and, in particular, at $\Delta_{12} = 0$), which is rather difficult for the ordinary pulse-saturation technique.

Experimental study of the cross relaxation has been carried out on ruby crystals with 0.035% Cr at $T_0 = 4.2$ K (14). The experimental details were described in Section III.B, a typical example being shown in Figure 5. Because of the strong thermal contact between the ESSR and the NZS (Section V.B) and, on the other hand, because of the large heat capacity c_{1Z} of the nuclear subsystem as compared to c_{SS} , the common spin temperature $T_{SS} = T_{1Z}$ does not change during the 50-Hz modulation used in monitoring the signals. Therefore, in this case $\beta_{SS} = \text{const}$, and at $\Omega \gg \tau_{CR}^{-1}$ the observed signal $\chi_{CR}''(\Delta_{12})$

(Figure 5) gives, according to Eq. (24), the shape of the cross-relaxation line $W_{CR}(\Delta_{12})$. This function, determined in this manner, was found to be close to a Gaussian produced by overlapping two EPR lines involved in cross relaxation, though a weak “tail” was also observed at larger Δ_{12} .

In the same paper (14) the dependence of χ_{CR}'' on the frequency Ω was investigated under conditions of the resonant cross relaxation (at $\Delta_{12} = 0$). The data are presented in Figure 13, and it is seen that the experimental points cannot be fitted to Eq. (22). This indicates that the relaxation law deviates from a single exponential and may be understood as a result of some spread of τ_{CR} values due to the random spatial distribution of paramagnetic ions (59). The theoretical curve calculated on this assumption is also shown in Figure 13; it agrees well with the experiment (the best fit was obtained with a mean τ_{CR} value of 0.8×10^{-6} s).

E. NMR in the Rotating Frame and the Suppression of the Dipolar Broadening in Solids

As mentioned in Section III.C, at $H_1 \gg H_L$ the dependence of χ_{S^*} on Ω takes the form of a resonance in the effective field H_e acting in the tilted rotating reference frame (TRF). In spite of the fact that the existence of such a resonance is rather obvious, for a long time it was investigated only indirectly, through various changes in “ordinary” NMR signals registered at high frequency ω_0 (26, 60) or by optical detection in gases (61). The direct

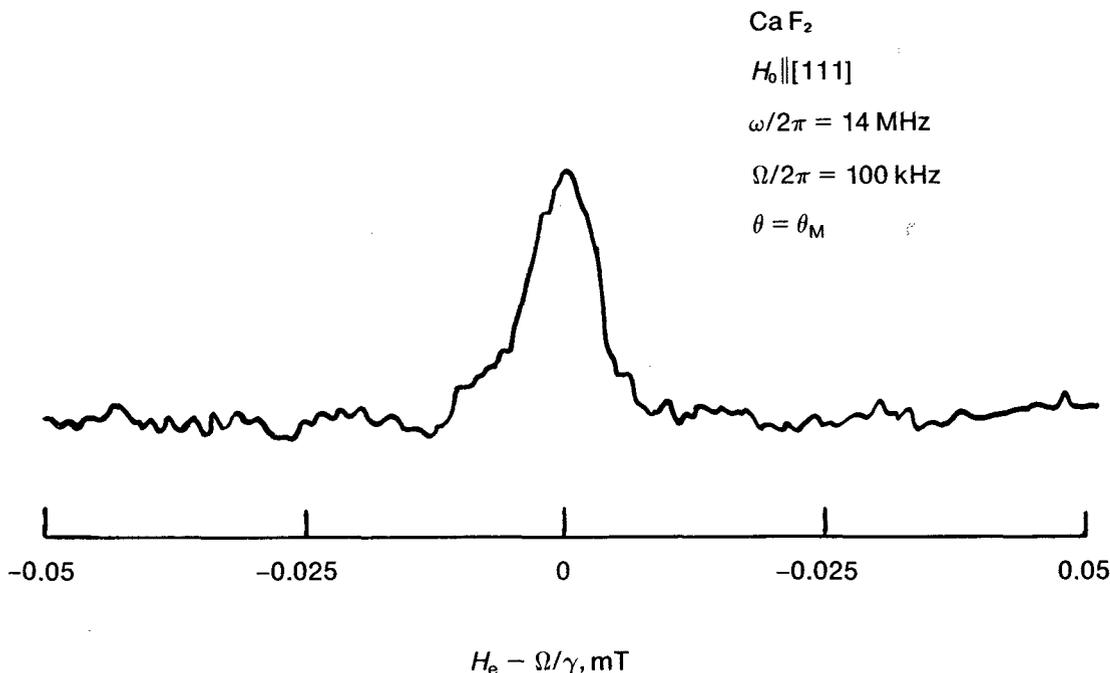


Figure 14. An oscillogram of the ¹⁹F NMR line in the tilted rotating reference frame, obtained at its natural frequency Ω_0 under “magic angle” conditions.

observation of NMR in TRF at its natural frequency $\Omega_0 = \gamma H_e$ has been realized only by the use of ELSE technique (18, 19, 21).

Figure 14 shows an oscillogram of the resonance absorption line taken of ¹⁹F nuclei in CaF₂ crystal ($H_L = 0.088 \text{ mT}$) with the aid of the longitudinally oriented pickup coil tuned to the frequency $\Omega_0 = 100 \text{ kHz}$. The half amplitude H_1 of the exciting rf field is in this case about 2.00 mT, so the resonance in the effective field is attained at a detuning $\Delta = \sqrt{\Omega_0^2 - (\gamma H_1)^2} \approx \gamma (1.40 \text{ mT})$ (see Figure 14).

The most interesting feature of this spectrum is that it was obtained under conditions of the so-called “magic angle” between H_e and the z-axis,

$$\theta = \theta_M = \cos^{-1} \left(\frac{1}{\sqrt{3}} \right)$$

It is known (26) that in this case the secular part of the nuclear dipole-dipole interaction vanishes (in the first-order perturbation theory), and hence a sharp decrease of the line width is expected. In fact, the width of the line shown in Figure 14 is equal to about 300 Hz, whereas in the laboratory frame it reaches 15 kHz.

The experimental procedure and the results obtained by this method, including the resolution of chemical shifts in solids, saturation of the resonance in the TRF, as well as the analysis of the “residual” line width at $\theta = \theta_M$ are described in detail in ref. (19). It is enough to say

here that the resolution is limited by dipole interaction in the second-order perturbation theory and by the inhomogeneity of the rf field.

The sensitivity of such low-frequency magnetic resonance is rather high, since almost the entire equilibrium magnetization M_{z0} attained in the field H_0 may be directed along the effective field H_e by the use of fast adiabatic passage (33). In addition, a further increase in the signal magnitude is due to considerable narrowing of the resonance line at $\theta = \theta_M$. It is curious that in Redfield’s fundamental paper (26) the opinion was advanced that direct observation of NMR in TRF is not possible at all because of the small absorption value at low frequencies. Now we see this pessimistic prediction disproved.

It is worthwhile to compare the above-described technique with the multiple-pulse method that is widely used in obtaining high-resolution NMR in solids (62). On the one hand, an obvious advantage of the low-frequency experiments is that they yield spectra of increased resolution without the need for complicated coherent pulse apparatus and for a Fourier transformation of the output signal. On the other hand, however, the ELSE technique is at present inferior to the multiple-pulse technique with respect to the attainable resolution. Thus, in order to compete successfully with multiple-pulse spectroscopy, the resolution of the low-frequency method must still be improved by at least an order of magnitude. Such research is now in progress.

VI. CONCLUSIONS

ELSE may be regarded as a sort of hybrid of the good old Leiden method and much more modern magnetic resonance. We dare to say that this "child" has inherited the best features of its "parents": the high information content of the former and the high sensitivity of the latter.

Indeed, despite its rather short history, ELSE has already provided us with a good deal of valuable information, often not available by other methods, on some fine aspects of spin dynamics and relaxation in solids. In particular, the use of ELSE ensures the most precise and convenient method for measuring the spin-spin interaction temperature, especially in electron spin systems, and this enables one to monitor the spin-spin reservoir in the course of various transient processes.

ELSE is practically universal: it has already been observed in EPR, NMR, and NQR and recently even in acoustic experiments as well (64).

Finally, ELSE signals are easily observable: their magnitude is quite large, while the appropriate experimental setup is not complicated, especially in comparison with current standards of contemporary magnetic-resonance spectroscopy. It is therefore anticipated that in the future ELSE will be widely used in investigating spin systems.

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