VERIFICATION OF THE SPIN-SPIN TEMPERATURE CONCEPT IN EXPERIMENTS ON SATURATION OF ELECTRON PARAMAGNETIC RESONANCE

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The shape of the EPR line of the Ce^{3+} ion in a $CaWO_4$ crystal is investigated at 1.8°K under saturation conditions with a shift relative to the line center. Effects predicted by the spin-spin temperature (T_{SS}) theory[1] are observed. In particular, stimulated emission in the EPR line wing was observed in the transient and stationary states. The effect strongly grows on moving from the wing to the center of the line under saturation conditions. A detailed analysis of the line shape and of transient and relaxation processes revealed satisfactory quantitative agreement between the theory based on the T_{SS} concept and the experimental data. The mean local field strengths (γH_L = 2.3 MHz) and the spin-lattice relaxation time for the spin-spin interaction reservoir ($\tau_1' \approx 0.5$ sec) are estimated. With increase of the inhomogeneous EPR line width due to increase of the angle θ between the magnetic field and the crystal axis from 0 to 20°, it is found that enhancement of the effects involving a shift of T_{SS} occurs. With further growth of θ ($\theta > 20°$) the effects become weaker and then disappear. The results are interpreted from the standpoint of the "spin packet" model with allowance for spin-spin temperature. It is concluded that the T_{SS} concept can be applied to inhomogeneous EPR lines provided the cross relaxation within the inhomogeneous line is rapid (compared with the spin-lattice relaxation).

1. INTRODUCTION

RECENTLY there has been developed a new approach to the problem of spin-spin interactions in solid paramagnets, connected with introducing a spin-spin temperature (T_{SS}). According to this concept, the energy of the spin-spin interactions (more accurately, its secular part) is regarded as a separate energy reservoir (SS) isolated from the Zeeman energy (Z) of the spins in an external magnetic field H_0, and characterized by its own proper temperature T_{SS}, which under certain conditions can differ greatly from the Zeeman spin temperature T_Z.

The theory of spin-spin temperature, developed initially as applied to the problem of magnetic-resonance saturation[1], was subsequently extended to a description of cross relaxation[2-4] and dynamic polarization of nuclei[5-8]. Since, however, initially the T_{SS} concept was developed only for lines that are homogeneously broadened as a result of dipole-dipole interactions, it found extensive application only in NMR, where it received experimental confirmation long ago (for example,[4]).

The question of the applicability of the T_{SS} concept to EPR has not yet been solved finally, although this problem is of considerable interest in view of the importance and unusual character of the effects predicted by the theory.

Starting with 1967, we have performed a number of experiments[9-11] in which we succeeded, using the T_{SS} concept, to interpret incontrovertibly the results of experiments on the EPR line shape, electron cross relaxation, dynamic polarization of nuclei (DPN), and nuclear spin-lattice relaxation in certain paramagnetic crystals. Other papers were also published, in which the T_{SS} concept was used to explain experimental data[12,13]. All these experiments were performed, however, on crystals whose lattices contained nuclear spins that influenced (especially under DPN conditions) the shape of the EPR line. In this connection, the interpretation of the experiments turned out to be quite complicated and frequently ambiguous. It was of interest to organize a "pure" experiment with a paramagnetic crystal without nuclear spins, and this was the purpose of the present work.

As the criterion for the applicability of the T_{SS} concept we chose an experimental verification of the theoretically predicted EPR line shape under conditions of "not strictly resonant saturation" (i.e., saturation at a frequency that differs somewhat from the central resonant frequency ν_0). According to the T_{SS} concept, when a quantum $h\nu' \equiv h(\nu_0 + \Delta)$ is absorbed, the energy $h\nu_0$ is transferred to the Z system, which has a single resonant frequency ν_0, and the "remainder" $h\Delta \ll h\nu_0$ falls into the SS system (or is extracted from it if $\Delta < 0$). The absorption coefficient in the contour of the homogeneously broadened line is determined in this case by the expression[1]:

$$P(\delta)=Ag(\delta)\left(\frac{\nu_0}{T_Z}+\frac{\delta}{T_{SS}}\right), \quad (1)$$

where $g(\delta)$ is the equilibrium line-shape function, δ is the running detuning relative to ν_0, and A is a proportionality coefficient. Under conditions of equilibrium with the lattice, $T_Z = T_{SS} = T_0$ and the contribution of the term δ/T_{SS}, which has the meaning of the Boltzmann factor of the SS system, is negligible, since $|\delta| \ll \nu_0$. On the other hand, if saturation occurs at the frequency ν', i.e.,

$$P(\Delta)=Ag(\Delta)\left(\frac{\nu_0}{T_Z}+\frac{\Delta}{T_{SS}}\right) \to 0, \quad (2)$$

then a strong deviation of the SS system from equilibrium takes place ($|T_0/T_{SS}| \gg 1$). In the case of sufficiently strong stationary saturation we have

$$\frac{T_0}{T_Z} = -\frac{\Delta}{\nu_0}\frac{T_0}{T_{SS}} = \left[1+\left(\frac{\Delta_0^\infty}{\Delta}\right)^2\right]^{-1}, \qquad (3)$$

where $(\Delta_0^\infty)^2 = (\gamma H_L)^2\tau_1/\tau_1'$; H_L^2 is the mean square of the local fields produced by the spins; γ is the spectroscopic splitting factor; τ_1 and τ_1' are respectively the spin-lattice relaxation times of the Z and SS systems.

The absorption line shape determined by expressions (1) and (3) is shown in Fig. 1. We see that the absorption coefficient in the line contour is not equal to zero, as would follow from the old theory[14], but has an appreciable magnitude, and $P(\delta)$ even exceeds its equilibrium value in a certain region. On the other hand, there appears a section where $P(\delta) < 0$ (stimulated emission), which is also very unusual.

We note that at the first instant after saturation is reached at the frequency $\nu_0 + \Delta$ (i.e., prior to the establishment of the stationary state and the appearance of the influence of the lattice) the line shape is described by the same formulas (1) and (3), except that Δ_0^∞ in (3) is replaced by $\Delta_0^0 = \gamma H_L$[3]. It is customarily assumed that $\tau_1' < \tau_1$; consequently, $\Delta_0^0 < \Delta_0^\infty$, and at the first instant the values of T_0/T_Z and $|T_0/T_{SS}|$ should be larger than in the stationary states.

A brief report of the first observation of the described effects in the nonstationary regime on the EPR line of the Fe^{3+} ion in $K_3Co(CN)_6$ crystals was published by us earlier[9]; in this paper we present results of a detailed experimental investigation, carried out on a more convenient object.

2. EXPERIMENTAL CONDITIONS

The model for the "pure" experiment on not strictly resonant saturation was chosen to be a $CoWO_4$ crystal with Ce^{3+} ions as an impurity. This substance does not contain nuclear spins; the effective spin of the Ce^{3+} ion is 1/2, which simplifies to the utmost the comparison of the theory with experiment; the time τ_1 at low temperatures is exceptionally large (τ_1 = 4 sec at $T_0 = 1.8°K$[15]). This makes it possible to avoid the difficulties connected with the rapid decay of the effect as a result of relaxation of the SS system to the lattice (see our experiments on $K_3Co(CN)_6 : Fe^{3+}$[9]). In addition, the half-width $(\Delta\nu)$ of the Ce^{3+} EPR line in $CaWO_3$ increases strongly with increasing angle θ between H_0 and the crystal axis (see the table in Sec. 3), so that it becomes possible to carry out the investigations at different contributions of inhomogeneous broadening.

The Ce^{3+} concentration in the investigated crystal, determined by the EPR method, was $\sim 10^{18}$ cm^{-3}. The experiments were performed at $T_0 = 1.8°K$ in the 3-cm band. The EPR line was observed on an oscilloscope with the magnetic field modulated at a frequency of 50 Hz. The not strictly resonant saturation at a fixed point of the line contour was produced by short (20–70 μsec) periodic microwave pulses turned on at the instant of passage over the required section of the line in synchronism with modulation of the magnetic field. The saturable section amounted to $\sim (\Delta\nu)/20$. In the intervals between the pulses, the line was observed with the aid of a sufficiently weak (unsaturated) microwave signal having the same frequency as in the pulses. Since the pulse repetition period (20 msec) was much shorter than τ_1, the periodic pulses ensured practically stationary saturation.

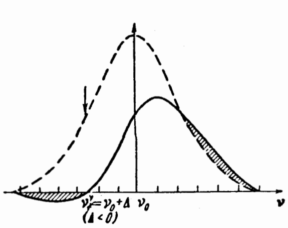

FIG. 1. Theoretical line shape of paramagnetic resonance under conditions of not strictly resonant saturation at a frequency $\nu' = \nu_0 + \Delta$. The regions of stimulated emission and of increased absorption are shaded. Dashed—equilibrium line shape.

The pulse power was chosen such that a single pulse produced an approximately 30% decrease of the absorption in the saturable section of the line; to obtain good saturation, 5–10 pulses were required, i.e., a time 0.1–0.2 sec. Such a choice of the saturation regime ensured satisfaction of the condition $H_1 \ll H_L$ (H_1—microwave field amplitude) needed for the applicability of the theory[1].

Particular attention was paid to elimination of the possible distortions of the EPR line shape resulting from the influence of paramagnetic resonant dispersion. This influence can be large if the microwave generator is detuned relative to the working cavity resonator (in this case the dispersion signal is antisymmetrical relative to the line center). When the generator is exactly tuned to the resonator, the dispersion should appear weaker and should be expressed in an increase of the reflection coefficient from the resonator symmetrically on both sides of the EPR line center (a spectroscope with a reflex resonator was used). In both cases the dispersion can bring about an EPR line shape close to that shown in Fig. 1 and lead to an error in the interpretation of the results.

To avoid this, all the experiments were performed alternately on both wings of the line, making it possible to monitor the influence of the antisymmetrical dispersion signal, and in addition were repeated at different coefficients of coupling between the resonator and the waveguide channel (above and below the critical value), making it possible to estimate the influence of the symmetrical dispersion signal. The experiments were repeated also at different values of the working-resonator Q, which also made it possible to monitor the influence of dispersion.

All the experimental results presented below were obtained under conditions when the dispersion did not exert a noticeable influence on the line shape, a fact verified each time by the methods indicated above.

3. EXPERIMENTAL RESULTS AND DISCUSSION

A. Not Strictly Resonant Saturation (Qualitative Results)

The EPR line shape was observed under conditions of not strictly resonant saturation at $\theta = 0–40°$ and at different values of the detuning Δ of the saturating signal relative to the center of the line. Certain oscillograms are shown in Figs. 2–5, where the index a corresponds to the first instant after reaching saturation at the frequency $\nu_0 + \Delta$ (i.e., 0.1–0.2 sec after turning on the saturating pulses), and the index b pertains to the stationary regime.

The main feature of Figs. 2—4 is the undisputed qualitative agreement between the observed line shape and the theoretical predictions (Fig. 1), namely, the absorption in the line contour differs from zero, and on the wing where the saturation takes place there is actually observed a section of negative absorption (stimulated emission). We see that when θ = 0 and 10° the effect of stimulated emission is maximal at the first instant (Figs. 2a and 3a) and is less clearly pronounced (especially for θ = 0) in the stationary regime (Figs. 2b and 3b), in full agreement with the theoretical predictions based on the T_{SS} concept (see the Introduction). At θ = 20°, to the contrary, in the stationary regime the effect increases (Fig. 4), and at θ = 40° there is no stimulated emission, and the line shape corresponds to the traditional ideas [16] concerning "hole burning" (Fig. 5).

The stimulated emission is observed most distinctly at θ equal to 10 and 20°.

All these features will be discussed in greater detail in the subsection E below, where we consider the role of the inhomogeneous line broadening. Here we only emphasize the fact that the occurrence of stimulated emission on the line wing is apparently indisputable evidence that the concept of spin-spin temperature is valid in EPR.

The very fact that we obtained stationary stimulated emission in a spin system with one resonance line is also quite interesting.

We note that a similar but much more clearly pronounced picture is observed in NNMR. For comparison, Fig. 6 shows the result of an analogous experiment performed by A. I. Mefed[1)] on F^{19} nuclei in a CaF_2 crystal at 4.2°K.

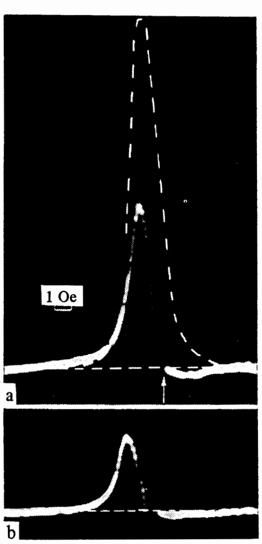

FIG. 2

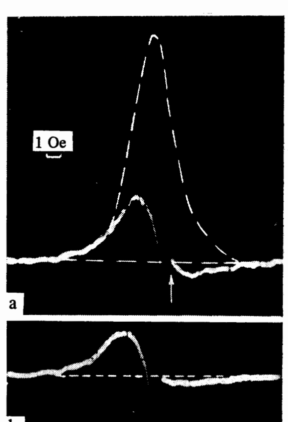

FIG. 3

FIG. 2. Oscillograms of EPR line of the Ce^{3+} ion in $CaWO_4$ under conditions of not strictly resonant saturation at θ = 0° (the saturation point is indicated by an arrow): a—at the first instant after saturation is reached at the point $\nu_0 + \Delta$; b—in the stationary regime. Dashed—level of zero absorption and equilibrium shape of the line.

FIG. 3. The same at θ = 10°.

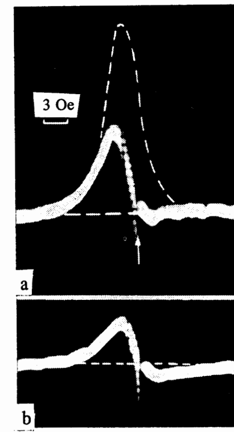

FIG. 4. The same at θ = 20°

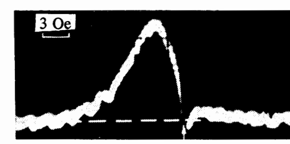

FIG. 5. Stationary EPR line shape at θ = 40°. The symbols are the same as in Figs. 2–4.

The EPR line shape (at θ = 0—20°) in the section where a residual positive absorption is observed also agrees qualitatively with the theoretical predictions. Here, however, another interpretation is also possible, based on the traditional concept of "spin packets" in an inhomogeneous line [16]. We have established that at θ equal to 0 and 10°, an increase of the power in the pulses in excess of the level necessary for good saturation at the frequency $\nu_0 + \Delta$ does not influence the line shape both at the first instant after saturation and in the stationary regime. This means that the observed residual absorption cannot be attributed to incomplete saturation of the wings of the corresponding "spin packets." The question of the possible role of "spectral diffusion" will be discussed below (in subsection D).

B. Stroboscopic Line Passage with Saturating Pulses

In spite of the success of the described experiments on not strictly resonant saturation, we consider it essential to carry out additional experiments, inasmuch as

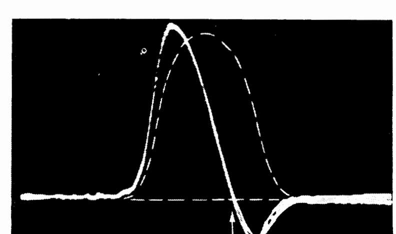

FIG. 6. Oscillogram of NPR line of F^{19} in CaF_2 at 4.2°K (first instant after saturation is reached). The symbols are the same as in Figs. 2–4.

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1)The author thanks A. E. Mefed for supplying Fig. 6 prior to its publication.

the effect of stimulated emission on the line wing turns out to be insignificant in magnitude (it was even more difficult to observe reliably the increase of absorption on the other wing, although this effect was nevertheless noted, see, for example, Figs. 2a and h).

The idea of increasing these effects consisted of producing saturation at the line center, i.e., at the point ν_0, immediately after the saturation at the frequency $\nu_0 + \Delta$. As a result, the Z system should be saturated ($T_0/T_Z = 0$), and the absorption line shape is determined only by the state of the SS system. As seen from (1), in this case there should be observed an antisymmetrical absorption signal $P(\delta) \propto g(\delta)\delta/T_{SS}$, where T_{SS}, as before, is determined from (3). Naturally, this experiment must be carried out within a time that is short compared with the spin-lattice times τ_1 and τ_1'.

In our experiments we use the following procedure. The first switching on of the saturating pulse was carried out at the instant of passage over the remote wing of the line, during the next period of modulation of the magnetic field the saturation was carried out closer to the line center, etc., until the spectrum itself was subjected to the saturation (we call such an operation "stroboscopic passage").

The oscillograms obtained by motion-picture photography at different instants of the stroboscopic passage are shown in Fig. 7. We see that after the passage the line actually has an antisymmetrical form (Fig. 7d); the stimulated-emission signal has increased considerably compared with Figs. 2—4. An analysis of the motion picture frames makes it also possible to establish that the magnitude of the absorption on the "left" line wing increases from Fig. 7a to 7c, and exceeds its equilibrium value. All these effects are clearly pronounced at $\theta = 0—20°$; with further increase of θ they vanish gradually.

To reach the maximum radiation signal, the time of passage was chosen to be equal to ~0.5 sec. Faster passage no longer ensured good saturation of the line, and in slower passage the effect decreased, apparently as a result of the influence of the spin-lattice relaxation of the SS reservoir.

The appearance of stimulated emission in stroboscopic passage cannot be attributed to the effect of adiabatic fast passage (AFP) of the entire line, after Bloch[17], since the passage time (~0.5 sec) and even the pulse repetition period (20 msec) exceed the reasonable values for the spin-spin relaxation time by several orders of magnitude.

Another possible interpretation of the observed effect might be the assumption of successive AFP of each spin packet when acted upon by an individual pulse. However, first, experiment has shown that a single pulse does not lead to inversion of the absorption on the corresponding line section. Second, stroboscopic passage of the line in a direction from the center to the wing gave no effect whatever, leading only to a weakening of the absorption signal. Finally, third, an analysis of the occurrence of stimulated emission at a certain fixed point of the line (corresponding to the vertical bar in Fig. 7) shows that the emission signal does not arise immediately after the action of the saturating pulse (frames a and b), but appears only a certain time after, reaching a maximum when the pulse approaches the line center (frames c and d). All this contradicts the assumption of inversion of the line "over the packets" and is in full agreement with the T_{SS} concept.

We note that even the results of Redfield[18], who first introduced the concept of a single spin temperature in a rotating coordinate frame, led to the possibility of obtaining stimulated emission in the case of "isentropic" passage that is rapid compared with τ_1 but not with τ_2. Heretofore, however, (see, for example,[19,20]), the interpretation of similar experiments in EPR was not connected with the T_{SS} concept[1]. As a rule, it was based on an utterly inconsistent mixing of the AFP concept after Bloch[17], which presupposes conservation of the phase of the precession of the magnetic moment about the effective field, with Redfield's thermodynamic theory[18], where the concept of the precession phase is not applicable at all.

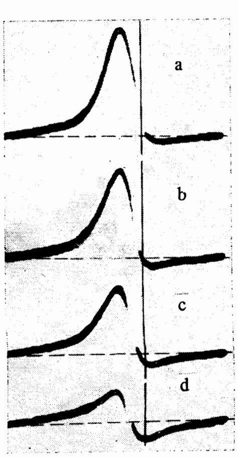

FIG. 7. Motion picture frames of stroboscopic passage of saturating pulses over the EPR line from the "right" wing to the center ($\theta = 10°$). The time between neighboring frames is 1/8 sec. The vertical line fixes the point of the line on which observations are made.

C. Not Strictly Resonant Saturation (Quantitative Results)

The experimental results described in subsections A and B offer serious evidence favoring the applicability of the T_{SS} concept to our case. We now proceed to a more detailed comparison of the experimental data with the theory.

We turn first to the line shape under conditions of not strictly resonant saturation. Substituting (3) in (1) we obtain

$$P(\delta) = P_0(\delta)\frac{T_0}{T_Z}\left(1 - \frac{\delta}{\Delta}\right), \tag{4}$$

where $P_0(\delta)$ is absorption under conditions of equilibrium with the lattice.

As can be seen from the solution of the rate equations for the Z and SS systems and for the lattice[3], expression (4) is valid for the entire period of time from the instant of attainment of good saturation at the frequency $\nu_0 + \Delta$ to the establishment of the stationary regime. All that changes in (4) is the quantity T_0/T_Z, which can thus be chosen in the form of a single parameter for the construction of the line shape at specified $P_0(\delta)$ and Δ.

In comparing formula (4) with experiment, the value of T_0/T_Z was determined from the value of the absorption of the frequency ν_0, referred to equilibrium absorption at the same point. Figure 8 shows the theoretical

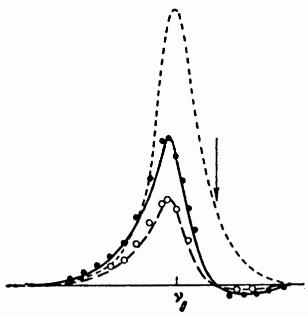

FIG. 8. Points–results of measurement of the oscillograms of the EPR line (θ = 10°) under saturation conditions at the place indicated by the arrow; curves–calculation in accordance with formula (4) with suitable choice of the parameter T_0/T_Z: ● and solid curve–at the first instant after saturation is reached; ○ and dashed curve–in the stationary régime; dotted line–equilibrium line shape.

curves corresponding to (4), together with the results of measurements of the experimental oscillograms obtained both at the first instant after saturation and in the stationary conditions (θ = 10°). It is seen that in both cases formula (4) describes the experimental data well.

Good agreement between the experimental line shape and (4) is obtained also for θ equal to 0 and 20° (in the latter case only for the stationary regime).

The dependence of T_0/T_Z on the detuning (Δ) of the saturating pulses relative to the line center is shown in Fig. 9 (θ = 0°). Besides the stationary values $(T_0/T_Z)_\infty$, there are shown also values of $(T_0/T_Z)_0$ obtained by extrapolating the experimental dependence of $T_Z(t)$ to the instant t = 0. Figure 9 shows also the theoretical curves corresponding to (3). The best agreement with the experimental data was attained at Δ_0^0 = 3.2 MHZ and Δ_0^∞ = 6.8 MHz. The values of Δ_0^∞ for other angles θ, obtained by the same method, are listed in the table (in subsection E).

It follows from the theory[3] that for homogeneously broadened lines we have $\Delta_0^\infty/\Delta_0^0 = (\tau_1/\tau_1')^{1/2}$. From this we get τ_1/τ_1' = 4.5, i.e., τ_1' = 0.9 sec. This value contradicts the results of the analysis of the transient process (see subsection D). It will be shown in subsection E that this discrepancy can be eliminated by taking into account the role of the inhomogeneous broadening of the EPR line.

	θ, deg				
	0	10	20	30	40
$\Delta\nu$, MHz	4.0	5.5	8.1	11.9	13.7
Δ_0^∞, MHz	6.8	8.1	11.2	—	—
$(M_2^*)^{1/2}$, MHz	2.27	4.82	9.16	—	—
$M_2'^{1/2}$, MHz	5.15	6.6	9.4	12.6	14.8

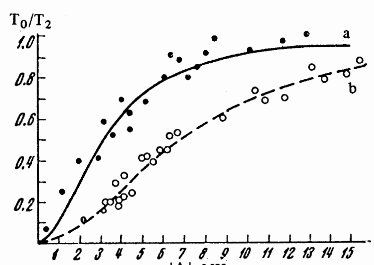

FIG. 9. Dependence of $(T_0/T_Z)_0$ (curve a) and $(T_0/T_Z)_\infty$ (curve b) on the detuning (Δ) of the saturation frequency relative to ν_0 (θ = 0°). Points–experiment, curves–calculation in accordance with formula (3) with parameters Δ_0^0 = 3.2 MHz and Δ_0^∞ = 6.8 MHz.

D. Transient and Relaxation Processes

Motion picture photography of the transient process in experiments on not strictly resonant saturation, carried out at θ equal to 0 and 10°, has shown that the process proceeds in two stages. In the first stage, which approximately coincides with the reaching of good saturation at the frequency $\nu_0 + \Delta$ (i.e., 0.1–0.2 sec), the line shape changes significantly, going from the equilibrium shape to the shape shown in Figs. 2a and 3a.

In the second stage there occurs a proportional change of all the sections of the line, i.e., a simple increase of the vertical scale. In particular, no change takes place here in the position of the maximum of the absorption curve. Such a behavior apparently contradicts the traditional concepts of "spectral diffusion"[16], which lead, as is well known, to a spreading of the "hole" and to the shift of the absorption maximum, but agrees fully with the T_{SS} concept (see formula (4) and Fig. 8).

During the second stage of the transient process, T_0/T_Z approaches the value $(T_0/T_Z)_\infty$ exponentially, with a time constant (τ'') that depends on Δ, ranging from 0.5 ± 0.1 sec as $\Delta \to 0$ to 4 sec when $\Delta \gg \Delta\nu$. According to a theoretical calculation based on the T_{SS} concept[3], the establishment of the stationary value of T_0/T_Z after reaching saturation at a frequency $\nu_0 + \Delta$ should also occur exponentially with a time constant $\tau''_{\text{theor}} \to \tau_1'$ as $\Delta \to 0$ and $\tau''_{\text{theor}} \to \tau_1$ as $\Delta \to \infty$. If it is assumed that this calculation is applicable in our case, then a comparison of τ'' with τ''_{theor} yields $\tau_1' \approx 0.5$ sec.

At θ = 0 there was investigated also the process of restoration of the equilibrium line shape after the removal of saturation, particularly after stroboscopic passage over the line from the wing to the center (see subsection B) and turning off the saturating pulses. Observation of the absorption at the point of the maximum of the curve in Fig. 7d has revealed two exponentials with time constants 0.6 ± 0.15 sec and 4.0 sec (after termination of the first of these exponentials, the line assumed a "normal" symmetrical form). If it is assumed that the first and second exponentials are due to the spin-lattice relaxations of the SS and Z systems respectively, then these time constants should correspond to the values of τ_1' and τ_1[3].

Thus, the processes of establishment and relaxation are described satisfactorily by the theory[3] if it is assumed that $\tau_1/\tau_1' \approx 8$. This result does not agree with the simplest theoretical estimates that yield $\tau_1/\tau_1' \approx 2$ (see, for example,[18]). The shortening of τ_1' apparently can be connected with the influence of uncontrolled paramagnetic impurities. When $\theta > 10°$ it is impossible to reconcile the experimental picture of the transients with the theory[3]. This is obviously connected with the inhomogeneous line broadening.

E. Analysis of the Data with Allowance for Inhomogeneous Line Broadening

Attempts have been made recently to apply the T_{SS} concept to the theory of saturation of an inhomogeneous line[21-24]. One of the possible approaches to this problem is to represent the inhomogeneous spin system in the form of an aggregate of homogeneous "spin packets" and taking into account the change of T_{SS} resulting both from the not strictly resonant saturation of each packet and from cross relaxation between packets.

In particular, it was shown[24] that under conditions of fast cross relaxation (compared with τ_1 and τ_1') between the packets one can expect effects close to manifestations of the shift of T_{SS} in the homogeneous line. In this case formulas (1), (3) and (4) remain valid, but it is now necessary to use the values

$$\Delta_0{}^0=[(\gamma H_L)^2+M_2{}^*]^{1/2}, \qquad \Delta_0{}^\infty=\left[\frac{\tau_1}{\tau_1'}(\gamma H_L)^2+M_2{}^*\right]^{1/2}, \qquad (5)$$

where M_2^* is the second moment of the distribution function of the number of spins over the packets relative to ν_0.

Assuming that in our case $\tau_1/\tau_1' = a$ (see subsection D) and choosing the values of Δ_0^0 and Δ_0^∞ from Fig. 9, we obtained from (5) the value $\gamma H_L \approx (M_2^*)^{1/2} = 2.27$ MHz for $\theta = 0°$. Using the obtained value of γH_L and the corresponding values of Δ_0^∞, we calculated M_2^* for θ equal to 10 and 20°. These results are listed in the table, which contains also the experimentally obtained values of $M_2^{1/2}$ (M_2—true second moment of the absorption line).

It is seen from the table that with increasing angle θ the value of $(M_2^*)^{1/2}$ approaches $M_2^{1/2}$ (the ratio of these quantities changes from 0.44 at $\theta = 0°$ to 0.97 at $\theta = 20°$), which undoubtedly agrees with the increasing role of the inhomogeneous broadening, a characteristic of which is precisely M_2^*. The ratio $\Delta_0^\infty/M_2^{1/2}$ also approaches unity (it changes from 1.32 to 1.19). The fact that it still remains larger than unity means, as seen from (5) that the term $\gamma H_L(\tau_1/\tau_1')^{1/2}$ makes an appreciable contribution, owing to the large value of τ_1/τ_1'.

We note that the value $\gamma H_L \approx 2.3$ MHz obtained by us agrees in order of magnitude with the theoretical estimate based on a direct calculation of M_2[25].

We did not determine Δ_0^∞ and M_2^* for $\theta > 20°$, since the line shape (Fig. 5) is no longer described by formula (4) in this case. Obviously, a transition takes place here to the case when the time of cross relaxation between the packets (τ_{cr}) turns out to be larger than τ_1. It is interesting that if $\tau_1' < \tau_{cr} < \tau_1$, then at the first instant after saturation is reached at the frequency $\nu_0 + \Delta$ it is necessary to expect the picture of "burned hole," whereas in the stationary regime the line should be approximately described by formula (4). Such a situation was indeed observed by us at $\theta = 30°$, and less distinctly also at $\theta = 20°$ (Fig. 4).

We note that when saturation was carried out very close to the line center, then the weakly pronounced "burned hole" was observed even at θ equal to 10 and 0°. In this case, however, the absorption in the line contour (on both sides of ν_0) was quite negligible. This obviously agrees with the fact that the ratio τ_{cr}/τ_1 always remains finite, although in this case the condition $\tau_{cr} \ll \tau_1, \tau_1'$ is satisfied.

The results enable us to draw the conclusion, unexpected at first glance, that the observation of new effects that follow from the T_{SS} concept, is carried out more conveniently in EPR with inhomogeneous lines. In fact, calculation of M_2 for a homogeneously broadened EPR line in dilute paramagnets[25] shows that in this case $\gamma H_L = (M_2/3)^{1/2} \gg \Delta\nu$. At the same time, as follows from (3), the maximum shift of T_{SS} can be reached in line saturation with $\Delta = \Delta_0 \gg \gamma H_L$. Thus, the point $\nu_0 + \Delta$ will correspond to a very remote wing of the homogeneous line, where it is difficult to ensure good saturation and it is practically impossible to observe the stimulated emission effect which takes place only when $|\delta| > |\Delta|$.

On the other hand, if the EPR is inhomogeneously broadened to such a degree that $\Delta\nu \sim \Delta_0 \sim \gamma H_L$, then the region of maximum effects falls within the limits of the line contour (of course, it is necessary here to satisfy the condition $\tau_{cr} \ll \tau_1$). In our case the ratio $\Delta\nu/\Delta_0^\infty$ changes from 0.59 at $\theta = 0°$ to 0.72 at $\theta = 20°$ (see the table); accordingly, the effect of the stationary stimulated emission also increases (Figs. 2b—4b). Further increase of the effect does not occur, obviously, owing to the slowing down of the cross relaxation within the line.

We note that in NMR, where there is no random distribution of the spins and therefore the ratio $\Delta\nu/\gamma H_L$ is much larger than in EPR, the effects connected with the shift of T_{SS} increase (Fig. 6).

4. CONCLUSIONS

The experiments have shown that the behavior of the EPR line of the Ce^{3+} ion in $CaWO_4$, under saturation conditions, agrees with the predictions of the theories[1,3,24], based on the concept of spin-spin temperature, and contradicts the traditional notions[14,16].

An important result of the investigation, in our opinion, is the conclusion that the T_{SS} concept can be applied to inhomogeneous EPR lines. We note that the "spin-packet" model used in[24] and by us is not perfectly rigorous; it is evidently necessary to develop further the theory of inhomogeneously broadened lines.

Observation of effects connected with the shift of the electron spin-spin temperature, under conditions of a "pure" experiment on a system with one type of spins, makes it now possible to carry out with greater assurance the corresponding interpretation of a number of interesting phenomena[10-13] observed in the study of electron cross relaxation, dynamic polarization of nuclei, and spin-lattice relaxation of nuclei in paramagnetic crystals. The application of the T_{SS} concept to inhomogeneous EPR lines will apparently explain also certain experimental results on dynamic polarization of nuclei in irradiated polymers[26] and on free radicals[27].

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