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TEMPERATURE OF SPIN-SPIN INTERACTIONS IN ELECTRON SPIN RESONANCE

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A review is presented of the theoretical and experimental papers on spin resonance, in which the concept of the reservoir of spin-spin interactions in a solid is used. We explain the main ideas connected with the introduction of two spin temperatures, T_Z and T_{SS}, to describe quasi-equilibrium in the Zeeman and spin-spin subsystems (Provotorov's theory); methods of strongly altering T_{SS} are indicated. We consider the effects due to the shift of the T_{SS} following saturation of the ESR line, dynamic polarization and spin-lattice relaxation of the nuclei, and electron cross relaxation both between different lines and inside lies with inhomogeneous broadening. Experiments show that the concept of spin-spin temperature in ESR are well confirmed and explain many new phenomena, namely induced emission at not too strong saturation of the ESR lines; polarization, relaxation, and thermal mixing of the nuclear spins by contact with the reservoir of the electronic spin-spin interactions; limitation of the redistribution of the saturation over the ESR spectrum in the case of cross relaxation; stimulated spectral diffusion, etc. It is shown that the shift of T_{SS} becomes equally manifest both in homogeneous ESR lines (with spin-spin broadening) and in inhomogeneous lines, provided only the spin-spin interactions are more effective than the spin-lattice ones.

CONTENT

INTRODUCTION

A new approach to the problem of the dynamic behavior of spin systems in a solid has been developed recently, and is based on segregating the energies of the relatively weak spin-spin interactions into a separate "reservoir" possessing its own temperature (T_{SS})[1,2] It turned out that the introduction of such a "spin-spin reservoir" (SS-reservoir) alters appreciably the traditional notions concerning the behavior of spin systems. In particular, it must be admitted that such well-established premises as the Bloembergen-Purcell-Pound saturation theory[3], the theories of cross relaxation[4] and spectral diffusion[5], the model of dynamic polarization of nuclei[6,7], and others, have limited applicability or are not applicable at all. On the other hand, the development of the spin-spin reservoir idea has led to the prediction of many new physical effects frequently quite unexpected, connected with saturation of the magnetic resonance lines, the redistribution of the excitation over the spectrum, electron-nuclear spin-spin interactions, and others.

The applicability of the concept of the SS-reservoir to nuclear magnetic resonance (NMR) was confirmed experimentally quite long ago (see, e.g.,[8-10]). In the case of electron spin resonance (ESR), however, such an

experimental verification has been greatly hindered. Consequently, the role of the spin-spin reservoir has been disregarded for a long time in ESR research (cf., e.g.[11-13]). Experiments pointing to the real existence and the great significance of the SS-reservoir in ESR were performed only very recently (1967–1971).

The present review is devoted mainly to just these latest results, although it does include a general section (Chaps. 1–2), aimed at describing the physical principles of the concept of spin-spin temperature and intended for a large group of physicists, whereas the second part of the review (Chaps. 3–6) is more specialized in character.

1. TEMPERATURE OF SPIN-SPIN INTERACTIONS

The object of the study of paramagnetic resonance in solids is usually the spin system in a crystal placed in an external magnetic field $\mathbf{H}_0$. If all the spins are the same, and if an alternating magnetic field with amplitude $2H_1$ and frequency ν is applied to the field H_0, then the Hamiltonian of the system is given by

$$\hat{\mathcal{H}} = h\gamma H_0 \hat{S}_z + h\gamma H_1 \hat{S}_x \cos 2\pi\nu t + \hat{\mathcal{H}}_{SS}; \qquad (1)$$

here $\hat{S}_Z$ and $\hat{S}_X$ are the operators of the sums of the projections of all the spins of the system along $\mathbf{H}_0$ and $\mathbf{H}_1$, respectively, $\gamma H_0 \equiv \nu_0$ and γH_1 are the Larmor frequencies of the spin precession around the fields $\mathbf{H}_0$ and $\mathbf{H}_1$, and γ is the spectroscopic splitting factor (in Hz/Oe). For simplicity we disregard for the time being the terms corresponding to the action of the intracrystalline field, and also the quadrupole and hyperfine interactions.

The first two terms in (1) constitute the Zeeman energy of the spins in the fields H_0 and H_1, respectively, and the third describes the spin-spin (magnetic dipole-dipole and exchange) interaction, which can be characterized by an rms local field H_L (cf., e.g.,[8,9,14]).

Under the conditions of paramagnetic resonance, we usually have $H_0 \gg H_1, H_L$, so that in the first approximation the eigenvalues of the Hamiltonian (1) are determined by the first term and correspond to a large number of degenerate equidistant levels separated by intervals $h\nu_0$. The spin-spin interaction lifts the degeneracy, splitting each level into a quasi-continuous band, the transitions within which correspond to frequencies of the order of γH_L.

In the traditional theory of paramagnetic resonance[3,14], it is assumed explicitly or implicitly that the probability n_i of finding the spin system at its energy level E_i is determined by the canonical distribution

$$n_i = \text{const} \cdot \exp(-E_i/kT_S), \qquad (2)$$

where T_S is called the spin temperature.

The establishment of the distribution (2), i.e., of the internal thermodynamic quasi-equilibrium with temperature T_S, is the result of spin-spin interactions during the spin-spin relaxation time τ_2, which is much shorter in solids than the spin-lattice relaxation time τ_1.

The introduction of the spin temperature has made it possible, in the solution of many problems, to regard (2) as a Boltzmann distribution of the populations in a simple two-level system corresponding to the spectrum of the individual spin in the field H_0. Using the population concept, we can describe the behavior of the spin system by means of simple rate equations that are widely used in all of the problems related to paramagnetic resonance (see, e.g.,[7,11-13]).

In particular, when saturation of resonance by an alternating field is considered, one speaks of an unbounded increase of T_S, meaning that the population difference tends to zero. To the contrary, a decrease of the field H_0, carried out rapidly in comparison with τ_1 but slowly in comparison τ_2 (so that quasi-equilibrium has time to set in "at each instant") decreases the energy gap $h\nu_0$ and leaves the population difference unchanged, meaning a decrease of T_S. It is interesting that such a demagnetization, all the way to $H_0 = 0$, is shown by experiment to be reversible, so that the magnetic moment of the system is completely restored when the field is subsequently increased. This means that this process is thermodynamically adiabatic, i.e., isentropic[14,15], and as $H_0 \to 0$ the spin ordering in the field H_0 is completely replaced by ordering in the local fields produced by the spins themselves; this effect reveals the deep physical meaning of the temperature T_S.

In spite of obvious success in the use of the concept of spin temperature, its introduction is not always valid. In fact, in order for an internal quasi-equilibrium to exist in a spin system it is necessary that its establishment time τ_2 be much shorter than the times of all the remaining interactions. This requirement is most obviously violated when $H_1 \gtrsim H_L$ and the action of the alternating field is no less effective than the action of $\hat{\mathcal{H}}_{SS}$. However, even when $H_1 \ll H_L$ (and this is precisely the case which we shall consider from now on) it is far from always that a single temperature T_S is established. The point is that when $H_0 \gg H_L$ direct energy exchange between the subsystems Z and SS, corresponding to the first and third terms in (1), has a rather low probability, owing to the strong difference between their natural frequencies ($\nu_0 \gg \gamma H_L$). Therefore, if we exclude the case $H_0 \sim H_L$, so that there are no obstacles to the establishment of a single temperature T_S, we can assume the subsystems Z and SS to be insulated from each other and neglect the nonsecular terms in the operator $\hat{\mathcal{H}}_{SS}$ (precisely as is done in the calculation of the absorption-line shape[16]). Thus, properly speaking, there are no grounds whatever for a single temperature T_S to exist in the joint spin system when $H_0 \gg H_L$, provided we do not deal with the trivial case of thermal equilibrium of the entire system with the lattice ($T_S = T_0$).

Nonetheless, by changing over to a coordinate system rotating with frequency ν around $\mathbf{H}_0$, Redfield[17] succeeded in reducing the problem of a strong saturation of paramagnetic resonance to the usual concept of a single spin temperature. In the rotating coordinate system, the alternating field $H_1 \cos 2\pi\nu t$ turns out to be static; when superimposed on the decreased (owing to the change of the coordinate system) constant magnetic field, it forms an "effective field" H_{eff}, with components $H^Z_{eff} = (\nu_0 - \nu)/\gamma$ and $H^X_{eff} = H_1$, which plays the role of the field H_0 in the rotating coordinate system. Consequently, in this system the Zeeman and spin-spin energies are comparable in magnitude, and a single spin

temperature T_S^* should be established there[17,18] in the case of strong saturation (when the interaction of the spins with the field H_1 is much stronger than with the lattice); naturally, this does not mean at all that a single spin temperature exists in the laboratory reference frame.

Redfield's theory was convincingly confirmed in experiments on strong NMR saturation in solids (see[17-20] and elsewhere), and made it possible, in particular, to explain the reversibility of the isentropic passage of the resonance line under saturation conditions[19]. In the general case of an arbitrary degree of saturation, however, it is no longer possible to retain the "single-temperature" description.

A solution of the problem was proposed by Provotorov[1], who used the concept of two generally different spin temperatures T_Z and T_{SS}, describing the quasi-equilibrium in each of the subsystems Z and SS (the latter corresponds to the secular part of $\hat{\mathcal{H}}_{SS}$, which will be denoted by $\hat{\mathcal{H}}_{SS}^0$). Such an approach, of course, presupposes the satisfaction of the inequalities

$$H_1 \ll H_L, \quad \tau_2 \ll \tau_1,$$

which express the requirement that the spin-spin interactions responsible for the establishment of the quasi-equilibrium be effective in comparison with the remaining interactions. We emphasize that in solids the first of these inequalities does not exclude by far the possibility of strong saturation, for which the condition $w\tau_1 \gg 1$ alone is sufficient (w is the probability of the transition induced by the field H_1), which is fully compatible with $H_1 \ll H_L$ when $\tau_1 \gg \tau_2$.

The described approach, which we shall call the "T_{SS} concept" for short, corresponds formally to the introduction of a quasi-equilibrium density matrix in the form

$$\hat{\rho}(t) = \text{const} \cdot \exp[-(\hat{\mathcal{H}}_Z/kT_Z) - (\hat{\mathcal{H}}_{SS}^0/kT_{SS})]. \qquad (3)$$

In paramagnetic resonance we usually have $h\nu \ll kT$, so that (3) can be linearized:

$$\hat{\rho}(t) \approx \text{const} \cdot [1 - (\hat{\mathcal{H}}_Z/kT_Z) - (\hat{\mathcal{H}}_{SS}^0/kT_{SS})].$$

At very low temperatures ($h\nu \gtrsim kT$), the ordering of the spin system increases sharply and a correlation appears between the states of the subsystems Z and SS, so that the question of the use of the T_Z and T_{SS} concepts calls for a special analysis[21].

The difference between the traditional concept of a unified spin temperature T_S and the T_{SS} concept is illustrated in Fig. 1, which shows the population distributions for both cases. We note that the reciprocal temperatures T_Z^{-1} and T_{SS}^{-1} characterize not only the average energies of the subsystems Z and SS, but also the degrees of their ordering, and an increase of $|T_Z^{-1}|$ corresponds to an ordering of the spins in the field H_0 ("with" and "against" the field), while an increase of $|T_{SS}^{-1}|$ corresponds to ordering in local fields (i.e., to spatial correlation in the spin orientation).

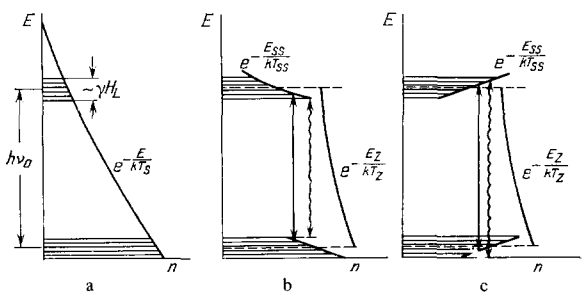

FIG. 1. Distribution of the populations n over the energy levels in models using a single spin temperature T_S (a) and two temperatures T_Z and T_{SS} (b, c).

The expression for the density matrix was used in[1] to obtain rate equations for T_Z and T_{SS}:

$$\frac{d}{dt}\frac{\nu_0}{T_Z} = -w(\Delta)\left(\frac{\nu_0}{T_Z} + \frac{\Delta}{T_{SS}}\right) - \frac{1}{\tau_1}\left(\frac{\nu_0}{T_Z} - \frac{\nu_0}{T_0}\right), \qquad (4)$$

$$\frac{d}{dt}\frac{\Delta}{T_{SS}} = -\frac{\Delta^2}{(\gamma H_L)^2} w(\Delta)\left(\frac{\nu_0}{T_Z} + \frac{\Delta}{T_{SS}}\right) - \frac{1}{\tau_1'}\left(\frac{\Delta}{T_{SS}} - \frac{\Delta}{T_0}\right);$$

Here $\Delta = \nu - \nu_0$, $w(\Delta) \propto \gamma^2 H_1^2 g(\Delta)$, where $g(\Delta)$ is the shape function of the equilibrium absorption line homogeneously broadened by spin-spin interactions, τ_1 and τ_1' are the spin-lattice relaxation times of the Z and SS reservoirs, respectively, and T_0 is the lattice temperature.

The coefficient $\mathcal{P}(\delta)$ of resonant paramagnetic absorption at a frequency $\nu_0 + \delta$ close to ν_0 turns out now to be proportional to the sum of the Boltzmann factors ν_0/T_Z and δ/T_{SS} that determine the population differences in the subsystems Z and SS;

$$\mathcal{P}(\delta) \sim g(\delta)[(\nu_0/T_Z) + (\delta/T_{SS})]. \qquad (5)$$

If the function $g(\delta)$ is symmetrical with respect to ν_0, the signal consists thus of a symmetrical and antisymmetrical part. It is clear that at $T_{SS} = T_Z$ (in particular, if $T_{SS} = T_Z = T_0$), the second term (5) is negligibly small because δ is small compared with ν_0, and we arrive again at the traditional concepts of the line shape[3,16]. However, if the conditions such that $|T_{SS}^{-1}| \gg |T_Z^{-1}|$ are produced, then formula (5) leads directly to an unusually and sharply asymmetrical shape of the absorption line.

This interesting result is only one of many consequences of the T_{SS} concept. Before we proceed to their analysis, let us stop to discuss the methods used to obtain a state with $|T_0/T_{SS}| \gg 1$.

2. METHODS OF VARYING THE SPIN-SPIN TEMPERATURE

We consider first the saturation of a magnetic-resonance line at a frequency $\nu = \nu_0 + \Delta \neq \nu_0$ ("not strictly resonant saturation"). Since the Zeeman subsystem has in our case a single resonant frequency ν_0, each act of absorption of a quantum $h\nu$ by the joint spin system should be accompanied by transfer of the "remainder" of the energy $h\Delta$ to the SS reservoir (or to extraction of an energy $|h\Delta|$ from it if $\Delta < 0$). Since the ratio of the specific heats of the spin-spin and Zeeman reservoirs is $C_{SS}/C_Z = (\gamma H_L)^2/\nu_0^2 \ll 1$, one can expect a sharp change of T_{SS} in the not-strictly-resonant saturation process. When $\Delta > 0$, the SS reservoir is "heated" until its upper energy levels are predominantly populated ($T_{SS} < 0$) (see Fig. 1c), and when $\Delta < 0$ it is "cooled" (see Fig. 1b).

This qualitative reasoning is confirmed by the solution of Eqs. (4). Under the conditions of strong saturation ($w(\Delta) \gg \tau_1^{-1}, \tau_1'^{-1}$) we obtain[22]

$$T_0/T_{SS} = -(\nu_0/\Delta)(T_0/T_Z) \approx -(\nu_0/\Delta)[1 + (\Delta_0/\Delta)^2]^{-1}, \quad (6)$$

where

$$\Delta_0 \equiv \Delta_0^\infty = \gamma H_L (\tau_1/\tau_1')^{1/2} \quad (7)$$

for the stationary regime and

$$\Delta_0 \equiv \Delta_0^0 = \gamma H_L \quad (8)$$

directly after the completion of the saturation, but before spin-lattice relaxation sets in (in the latter case it is assumed that $T_Z = T_{SS} = T_0$ prior to saturation). It is seen from (6)–(8) that the maximum of $|T_0/T_{SS}|$ is reached at $\Delta = \Delta_0$ and is equal to

$$|T_0/T_{SS}|_{max} = \nu_0/2\Delta_0, \quad (9)$$

i.e., the growth of $|T_{SS}^{-1}|$ should amount to two or three orders of magnitude and can be maintained in the stationary regime if the ratio τ_1/τ_1' is not too large (it is frequently assumed to be equal to 2–3[14]).

The value of $|T_0/T_{SS}|$ can be doubled in comparison with (9) if, by starting the strong saturation at $|\Delta| \gg \gamma H_L$ and ensuring it at each instant of time, we decrease Δ continuously to zero (the entire procedure is carried out with the system insulated from the lattice, i.e., rapidly in comparison with τ_1 and τ_1'). This process, called "adiabatic demagnetization in rotating frame" (ADRF), is more conveniently described in terms of Redfield's theory[17], which gives at $H_1 \ll H_L$ the same results as Provotorov's theory in strong saturation. In rotating coordinates, the decrease of Δ to zero means a corresponding decrease of H_{eff}, and the ADRF turns out to be analogous to the adiabatic (isentropic) demagnetization in the laboratory frame (see Chap. 1), namely, the spin ordering in the external field (in the field H_{eff} in the case of ADRF) goes over in both cases into ordering in the local fields.

T_{SS} can be varied also by cross relaxation, which consists of energy exchange between the Z and SS subsystems, due to the action of the nonsecular part of the operator $\hat{\mathcal{H}}_{SS}$. In fields $H_0 \gg H_L$, the cross relaxation time τ_{CR} may turn out to be shorter than τ_1 only if the spectrum contains several resonant lines whose frequencies ν_α, ν_β, ..., are either almost equal or almost integral multiples. The elementary act of first-order cross relaxation consists of simultaneous flipping of the near-equal-frequency spin systems α and β in opposite directions; it is obvious that the energy difference $h\Delta_{\alpha\beta} \equiv h(\nu_\beta - \nu_\alpha)$ should in this case be transferred to the common SS reservoir, causing thereby a change of T_{SS} (it is assumed here, naturally, that $\tau_{CR} \gg \tau_2$).

The change of T_{SS} by cross relaxation was calculated in[2], where rate equations were obtained for T_{SS} and the Zeeman temperatures $T_{Z\alpha}$ and $T_{Z\beta}$. If one of the Zeeman subsystems (e.g., Z_α) is saturated by the alternating field and if $\tau_{CR} \ll \tau_1, \tau_1'$, then the stationary values of T_0/T_{SS} and $T_0/T_{Z\beta}$ are given by formulas[22] that are similar to (6) except that Δ is replaced by $\Delta_{\alpha\beta}$ and the parameter Δ_0^∞ is replaced by

$$\Delta_0^{CR} = \gamma H_L [(\tilde{N}/\tilde{N}_\beta)(\tau_1^{(\beta)}/\tau_1')]^{1/2}, \quad (10)$$

where $\tilde{N}_{\alpha,\beta} = N_{\alpha,\beta} S_{\alpha,\beta}(S_{\alpha,\beta} + 1)$, $\tilde{N} = \tilde{N}_\alpha + \tilde{N}_\beta$, $N_{\alpha,\beta}$ and $S_{\alpha,\beta}$ are respectively the numbers and magnitudes of the spins of the particles of type α and β, while γ and H_L are averaged over all the spins having the common SS reservoir[8,9,14]. Thus, in this case, too, $|T_{SS}^{-1}|$ should undergo an increase which is almost as appreciable as in the case of not strictly resonant saturation. We note that the analogy between these two methods of acting on the SS reservoir (not-strictly-resonant saturation of a homogeneous line and saturation of one of the lines taking part in the cross relaxation) turns out to be quite far reaching (see Chap. 6).

Principally different methods for increasing $|T_{SS}^{-1}|$ were proposed by Jeener et al.[9] In one of these methods ("adiabatic demagnetization followed by sudden magnetization") the ordering of the spins in the local fields is attained by adiabatically decreasing the field H_0 to zero (see Chap. 1); this produces a single and rather low spin temperature T_{SS}. If the subsequent new application of the field H_0 is sufficiently rapid (not adiabatic), then this ordering is maintained, but characterizes only the SS reservoir, with T_S turning into T_{SS}. We note that this method, as well as another one (the method of two pulses[9]) was used so far only in MMR.

Thus, there are several methods for altering T_{SS} strongly. However, the manifestations of such a change were initially investigated only in MMR experiments, where the lines are usually broadened (homogeneously) by the spin-spin interaction, and therefore the Redfield-Provotorov theory is directly applicable (see, e.g.,[8-10,14,17-20]). The random character of the distribution of the paramagnetic impurity in electronic paramagnets, and particularly the important role played in ESR by the inhomogeneous line broadening (owing to imperfection of the crystal, the hyperfine structure (hfs) due to the interaction with the nuclear spins of the paramagnetic ions in the lattice, and others), have cast doubts for a long time on the applicability of the T_{SS} concept to electron spins. Recently, however, a number of ESR experiments (see[23-25] et al.) have revealed effects connected with the existence of an electron SS reservoir. They turned out to be even more interesting than in MMR, owing to the larger role played by cross relaxation in ESR, and also in connection with the observation of new mechanisms of dynamic polarization and spin-lattice relaxation of the nuclei in paramagnetic crystals. We proceed now to describe these results.

3. ESR LINE SHAPE UNDER SATURATION CONDITIONS

The ESR line shape in saturation can be investigated experimentally in two ways:

a) The line is saturated at a definite point of its contour (at the frequency $\nu = \nu_0 + \Delta$), and the remainder of the line is recorded with a sufficiently weak (nonsaturating) microwave signal.

b) The saturation and recording are carried out with the same microwave signal.

Method (a), in spite of its being somewhat more complicated, is preferable because the recorded absorption line shape $\mathcal{P}(\delta)$ characterizes here directly the state of the spin system, i.e., the population of its energy levels.

Expressing T_{SS} in terms of T_Z from (6) and substituting in (5) we obtain

$$\mathcal{P}(\delta) = \mathcal{P}_0(\delta)(T_0/T_Z)/[1 - (\delta/\Delta)], \quad (11)$$

Where T_Z is determined from (6) and $\mathcal{F}_0(\delta)$ is the value of $\mathcal{F}(\delta)$ at $T_Z = T_{SS} = T_0$. The line shape defined by (11) is shown in Fig. 2 (the equilibrium line is shown dashed; the regions of negative and increased absorption are shaded). We see that, in contrast to the traditional theory[3], according to which the saturation at any point of the contour of a homogeneous line leads to $\mathcal{F}(\delta) \to 0$ for all δ, now $\mathcal{F}(\delta)$ vanishes only at the saturation point ($\delta = \Delta$). The most interesting features of Fig. 2 are the regions of negative absorption (i.e., of induced emission) and of increased absorption (in comparison with $\mathcal{F}_0$) on opposite wings of the line[22]. The occurrence of these sections follows directly from the population distributions shown in Figs. 1b and 1c (the solid arrows on Figs. b and c show the saturation points $\Delta < 0$ (b) and $\Delta > 0$ (c), and the wavy lines show the induced emission signal on the line wing).

It should be noted that formula (11) holds true for any instant of time T after completion of the saturation at the frequency $\nu_0 + \Delta$;[22] in this case T_Z is obviously a function of t, since the parameter Δ_0 in (6) changes from Δ_0^0 to Δ_0^∞ during the course of the spin-lattice relaxation of the Z and SS reservoirs.

It is clear from (5) that the restoration of the equilibrium line shape after turning on the saturating signal should follow two exponentials: the antisymmetrical component, which is proportional to T_{SS}^{-1}, will vanish with a time constant τ_1', and the symmetrical (Zeeman) component will tend to $\mathcal{F}_0(\delta)$ with a time constant τ_1. Since usually $\tau_1' < \tau_1$, the first process is completed ahead of the second one.

The first experiments in which the effects illustrated in Fig. 2 could be observed were apparently performed in[23] on $K_3Co(CN)_6$ crystals with 0.6% Fe^{3+} ions (effective spin 1/2) as an impurity at 1.8°K in the 3-cm band. Saturation at the frequency $\nu_0 + \Delta$ was produced by short microwave pulses at $H_1 \ll H_L$, and the line was registered in the intervals between the pulses with the aid of a weak continuous microwave signal with a magnetic-field sweep that was rapid in comparison with τ_1. Sections of induced radiation and of increased absorption were observed on the line wings and were in sufficiently good agreement with relations (6) and (11), thereby justifying the conclusion that the T_{SS} concept can be applied in principle to ESR.

More detailed investigations of this type were performed on $CaWO_4$ crystals containing 10^{18} cm^{-3} Ce^{3+} ions (effective spin 1/2)[31]. Figure 3 shows some experimental results obtained at 1.8°K in the 3-cm band; we see that they agree well with formula (11), at the first instant after the saturation (1) as well as in the stationary regime (2). (The points represent the experimental data, curves 1 and 2 are theoretical (see formula (11)), and 3 is the equilibrium line.) An investigation of the dependence of T_Z and T_{SS} on Δ and an analysis of the establishment of the stationary saturation and of the spin-lattice relaxation[31] have also confirmed the conclusions of the theory, particularly the relation (6).

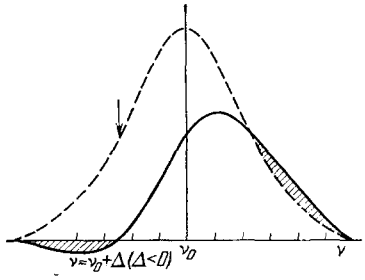

FIG. 2. The theoretical absorption-line shape $\mathcal{F}(\delta)$ under conditions of saturation at the frequency $\nu_0 + \Delta$ (arrow).

As seen from Fig. 3, the effect of induced radiation at not too strictly resonant saturation is relatively small. This is due to the fact that to obtain a maximum value of $|T_0/T_{SS}|$ it is necessary to saturate a line with a frequency deviation $\Delta = \Delta_0 \gtrsim \gamma H_L$, and in dilute paramagnets γH_L greatly exceeds the half-width of the homogeneous line[36]; as a result, the point $\nu_0 + \Delta_0$ turns out to be on the far wing of the line, where $\mathcal{F}(\delta)$ is very small. We note that in MMR, where the line shape is close to Gaussian and $\gamma H_L \sim \delta\nu$, the radiation on the wing turns out to be much stronger[37].

The radiation can be increased by saturating the line first on the wing and then at the center. Such a procedure, carried out within a time $t \ll \tau_1, \tau_1'$ causes the Zeeman energy to vanish ($T_0/T_Z = 0$) and the signal $\mathcal{F}(\delta)$, as seen from (5), should become antisymmetrical relative to the line center. This result was also obtained experimentally in[31]; the appearance of induced radiation when the saturation point is moved from the wing to the center of the line is illustrated by motion-picture frames (see Fig. 4, where the frames follow each other in intervals of 1/8 sec, and the vertical line marks the point of saturation at the instant a).

The experiment illustrated in Fig. 4 is close to the ADRF phenomenon mentioned in Chap. 2 and observed earlier in MMR[20]. Further motion of the saturation

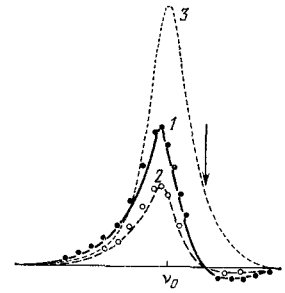

FIG. 3. ESR absorption line shape of the ion Ce^{3+} in $CaWO_4$ in the case of saturation at the point marked by the arrow.

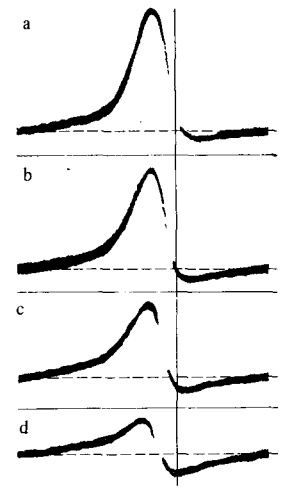

FIG. 4. Change of ESR absorption line shape of the ion Ce^{3+} in $CaWO_4$ when the saturation point is shifted (breaks in the curves) from the wing (a) of the line to its center (d).

point along the line (all the way to the opposite wing) gives a symmetrical absorption curve, but inverted relative to $\mathcal{P}_0(\delta)$. This phenomenon is also described in the case of NMR[19,20] and constitutes adiabatic (in the thermodynamic sense, i.e., isentropic) passage of the line[14,15]; it must not be confused with the fast adiabatic (in the quantum-mechanical sense) passage described by Bloch[38]. To obtain inversion in the latter case, it is essential to have synchronous precession of all the spins of the sample about the direction of the effective field in the rotating coordinate system; obviously, the passage must be completed within a time $t \ll \tau_2$, and the field H_1 should be much stronger than H_L. For the experiment to be successful in our case, the conditions are just the opposite, since it is assumed that there exists a single temperature T_S^* at each instant of time of the isentropic passage in the rotating coordinate system (see Chap. 1); this is connected with the total loss of synchronism in the motion of the spin and we should therefore have $t \gg \tau_2$ and $H_1 \lesssim H_L$ (and in particular also $H_1 \ll H_L$).

It should be noted that inversion of the absorption line, for passage within the time $t > \tau_2$, was observed in ESR also earlier. Then, however, this effect was not connected with the isentropic character of the passage, and was explained by an incorrect combination of Bloch's equations[38] with the results of Redfield's theory[17] (cf., e.g.,[11-13,39]).

In the cited papers[23,31], the effects confirming the T_{SS} concept were observed on lines whose shape was determined not only by the spin-spin interactions, but also, to no less a degree, by the inhomogeneous broadening. In[28], experiments similar to those described above were performed on the crystals $(Ce_xLa_{1-x})_2Mg_3(NO_3)_{12} \cdot 24H_2O$ ($x = 0.36 - 1$), where the width of the ESR line was determined practically entirely by the spin-spin interactions of Ce^{3+}. In these experiments, an agreement was also established between the line shape $\mathcal{P}(\delta)$ at not-strictly-resonant saturation and formula (11); in particular, induced radiation was observed on the line wing.

An interesting feature of the latter experiment was the occurrence of "phonon overheating" due to the strong coupling of the spin system with phonons having the same frequency as the ESR signal ("direct processes" of spin-lattice relaxation; cf., e.g.,[40]). To take this phenomenon into account from the point of view of the T_{SS} concept, the authors of[28] have proposed that phonon production in direct spin-lattice processes depends on the states of both spin subsystems Z and SS and is determined, just as resonant absorption of microwave energy, by the shape of the $\mathcal{P}(\delta)$ curve shown in Fig. 2 (more accurately, by the deviation of $\mathcal{P}(\delta)$ from $\mathcal{P}_0(\delta)$). This means that the phonon "temperature" $T_{ph}(\delta)$ varies within the limits of the ESR line, namely, it remains equal to T_0 at the point of intersection of $\mathcal{P}(\delta)$ with $\mathcal{P}_0(\delta)$ (see Fig. 2), but one should even expect it to decrease in the region of increased absorption. On the other hand, it is known that under "phonon overheating" conditions the spin-system state that leads to negative absorption (i.e., to emission) of the microwave-field energy can cause a very strong increase of T_{ph} (the so-called "phonon avalanche"[41]). Allowance for the change of T_{ph} has made it possible to explain in[28] certain deviations of the experimental data from the predictions of the theory[1].

An effective result was obtained in Kazan', where T_{ph} for the same crystals was determined directly by the Mandel'shtam-Brillouin scattering method using a laser[42]. Under the conditions of not-strictly-resonant saturation of the ESR line of the Ce^{3+} at 1.5°K, a "phonon avalanche" was observed, leading to a stationary increase of T_{ph} to 250°K at the ESR frequency, and to 8000°K in the pulsed regime. It is interesting that this effect, which is of appreciable magnitude, is apparently the consequence of a relatively weak signal of induced radiation on the line wing.

The difference between the traditional theory[3] and the T_{SS} concept should become manifest also in experiments on the registration of the line shape by the microwave saturating signal itself, i.e., using the method (b). In this case the absorption coefficient (i.e., the imaginary part χ'' of the paramagnetic susceptibility) is not so explicitly connected with T_Z and T_{SS}; to find it we can use the balance between the microwave field energy absorbed by the spin system at the frequency $\nu = \nu_0 + \Delta$ and the energy transferred to the lattice as a result of spin-lattice relaxation. Since the latter can be easily shown to be determined only by the deviation of T_Z from T_0, we have in the case of strong saturation[1,14,28]

$$\chi''(\Delta) = (H_0^2/P_{inc}\tau_1)\,\chi_0\,[(T_0/T_Z) - 1], \qquad (12)$$

where χ_0 is the static paramagnetic susceptibility at the temperature T_0, and P_{inc} is the microwave power incident on the sample.

The traditional theory[3] also leads to the formula (12), but then T_Z should be taken to mean the single spin temperature T_S. Since T_S, and consequently also χ'', does not depend on Δ in this case, formula (12) signifies an unlimited increase of the line width upon saturation. On the other hand, by substituting in (12) the expression (6) for T_Z, we see that in this case the absorption line should have a Lorentz shape with a half-width Δ_0^∞.

The use of the T_{SS} concept in the calculation of the real part of the paramagnetic susceptibility χ', which is proportional to the registered dispersion signal, also gives results that differ from the traditional theory. Thus, the assumption that in the case of strong saturation the total magnetic moment **M** of the spin system differs from zero and is directed along $\mathbf{H}_{eff}$ in a rotating coordinate system[17,18] leads directly to the conclusion that the component M_x, which is proportional to χ', also differs from zero. Simple calculation yields for this case

$$\chi' = -\chi_0\,(\nu_0/\Delta)\,[1 + (\Delta_0/\Delta)^2]^{-1},$$

and the dispersion signal thus does not tend to zero as $P_{inc} \to \infty$, i.e., it is not saturated.

Experiments on the registration of the absorption line shape with a saturating signal were carried out on a number of crystals with spin-spin broadening of the ESR line, namely, in a complex compound of divalent copper (without diamagnetic dilution) at 4.2°K[26], in cerium-magnesium double nitrate (both concentrated and diluted with diamagnetic lanthanum ions) at 1.4°K[28], and in diamond crystals with nitrogen-atom impurity at room temperature[35]. The results of all these experiments are well described (12) and thus confirm the "T_{SS} concept."

The conclusions of the Redfield-Provotorov theory were confirmed also in investigations of the signal of paramagnetic dispersion of χ' in ruby[26] and in carbonized dextrose[43] (in the latter case, however, the experiment was performed only at $H_1 \gtrsim H_L$).

4. ELECTRON-NUCLEAR INTERACTIONS

The concept of electron spin-spin temperature T_{SS} permits a new approach to the question of dynamic polarization of nuclei (DPN) and their spin-lattice relaxation in crystals with paramagnetic impurities.

In the magnetic fields customarily employed in practice (10^3—10^4 Oe), and at paramagnetic-center concentrations 10^{18}—10^{19} cm^{-3}, the MMR frequency for most nuclear spins falls in the same frequency band as the rate of electron spin-spin relaxation: $\nu_n \sim \tau_{2e}^{-1}$ 10^6—10^7 sec^{-1} (the subscripts n and e will henceforth denote the nuclear and electronic systems, respectively). This agreement causes the alternating local fields produced by the electron spins to have in their frequency spectra an appreciable component of frequency ν_n, which induces transitions in the nuclear Zeeman system Z_n. The "intermediary" between the electrons and the nuclei is in this case the electron-nuclear magnetic dipole-dipole interaction, the operator of which does not commute with the Hamiltonians of the systems SS_e and Z_n[44].

From the assumed existence of quasi-equilibrium in each of the systems SS_e and Z_n, it follows that such an exchange of energy between them is equivalent to a dire direct thermal contact with a tendency towards equalization of the temperatures T_{SS} and T_{Zn} of these reservoirs. If we increase $|T_0/T_{SS}|$ in some manner (not strictly resonant saturation of the ESR line, cross relaxation, etc.; see Chap. 2), then the direct thermal contact of the nuclear spins with the electronic SS reservoir should lead to a corresponding growth of $|T_0/T_{Zn}|$, i.e., to DPN[21,44,45]. This DPN mechanism is sometimes called "dynamic cooling" of the nuclear spins[21].

To describe the rate of establishment of thermal equilibrium between SS_e and Z_n, one introduces the times τ_{Sn} and τ_{nS}, which characterize respectively the relaxation of the SS_e system to Z_n and vice versa. It is easy to show[45] that

$$\tau_{Sn}/\tau_{nS} = C_{SS}/C_{Zn} = (N_e/N_n)\,[(\gamma H_L)^2/\nu_n^2]\,[S\,(S+1)/I\,(I+1)], \quad (13)$$

where N_e, S and N_n, I are the numbers and the spins of the electrons and nuclei, respectively, and C_{SS} and C_{Zn} are the specific heats of the systems SS_e and Z_n.

To calculate the time τ_{nS} we can use the well known theory of spin-lattice relaxation of nuclei in crystals with paramagnetic impurities[46,47]. Since, however, the system Z_n exchanges energy in this case not with the lattice but with the electronic SS reservoir, the correlation time τ_c of the quantity S_Z, which we need for the calculation, should be determined not by the spin-lattice but by the spin-spin relaxation of the electrons, i.e., it is of the order of τ_{2e} and not τ_{1e}.

Using the results of[47], we can obtain

$$\tau_{ns} = \frac{5}{2}\,(H_0/\overline{\delta H})^2\,a\tau_{2e}\,[1+(2\pi\nu_n a\tau_{2e})^{-2}], \quad (14)$$

where $\overline{\delta H}$ is the rms local magnetic field produced by the electrons at the locations of the nuclear spins (the averaging method is determined by the details of the spin-diffusion process[47]) and $a = \tau_c/\tau_{2e} \approx 3$[36,48].

In addition to the described direct thermal contact of the systems SS_e and Z_n, there is also another possibility of equalizing the temperatures T_{SS} and T_{Zn}, connected with the saturation of "forbidden" electron-nuclear transitions at the frequency $\nu_e + \nu_n$ or $\nu_e - \nu_n$ by means of a microwave field. As is well known, such a saturation leads in itself to DPN (the "solid state effect"[6,7]); it is shown in[49-51] that if the same microwave field saturates simultaneously also the main ("allowed") ESR line (this is possible if $\nu_n \lesssim \delta\nu_e$), then the nuclear-spin temperature T_{SS} is determined in this case by the conditions of not-strictly-resonant saturation at the frequency $\nu_e + \Delta$. In this mechanism, the role of the "intermediary" between SS_e and Z_n is played by the microwave field that saturates the "forbidden" transitions, and the rates of relaxation of SS_e to Z_n and vice versa turn out to be respectively of the order of $w_e^{\pm}$ and $w_n^{\pm}$, where

$$w_e^{\pm} = [N_n I\,(I+1)/N_e S\,(S+1)]\,w_n^{\pm} = (\overline{\delta H}/H_0)^2 w_e$$

is the probability of the "forbidden" transition.

Taking into account both mechanisms of coupling of the SS_e and Z_n reservoirs, we can write down rate equations for the temperatures T_{Ze}, T_{SS}, and T_{Zn}[45,25]:

$$\left.\begin{aligned}
\frac{d}{dt}\frac{\nu_e}{T_{Ze}} &= -w_e\left(\frac{\nu_e}{T_{Ze}}+\frac{\Delta}{T_{SS}}\right) - w_e^{+}\left(\frac{\nu_e}{T_{Ze}}+\frac{\nu_n}{T_{Zn}}+\frac{\Delta-\nu_n}{T_{SS}}\right) - \\
&\qquad -\frac{1}{\tau_{1e}}\left(\frac{\nu_e}{T_{Ze}}-\frac{\nu_e}{T_0}\right), \\
\frac{d}{dt}\frac{1}{T_{SS}} &= -\frac{\Delta}{(\gamma H_L)^2}\,w_e\left(\frac{\nu_e}{T_{Ze}}+\frac{\Delta}{T_{SS}}\right) - \frac{\Delta-\nu_n}{(\gamma H_L)^2}\,w_e^{+}\left(\frac{\nu_e}{T_{Ze}}+\frac{\nu_n}{T_{Zn}}+\frac{\Delta-\nu_n}{T_{SS}}\right) - \\
&\qquad -\frac{1}{\tau_{Sn}}\left(\frac{1}{T_{SS}}-\frac{1}{T_{Zn}}\right) - \frac{1}{\tau_{1e}'}\left(\frac{1}{T_{SS}}-\frac{1}{T_0}\right), \\
\frac{d}{dt}\frac{\nu_n}{T_{Zn}} &= -w_n^{+}\left(\frac{\nu_e}{T_{Ze}}+\frac{\nu_n}{T_{Zn}}+\frac{\Delta-\nu_n}{T_{SS}}\right) - \frac{1}{\tau_{nS}}\left(\frac{\nu_n}{T_{Zn}}-\frac{\nu_n}{T_{SS}}\right) - \\
&\qquad -\frac{1}{\tau_{nl}}\left(\frac{\nu_n}{T_{Zn}}-\frac{\nu_n}{T_0}\right),
\end{aligned}\right\} \quad (15)$$

where τ_{nl} is the time of the nuclear spin-lattice relaxation due to any mechanism with the exception of thermal contact between the systems Z_n and SS_e. It is assumed here that $\Delta > 0$, so that $w_e^- \ll w_e^+$.

The meaning of these equations is illustrated in Fig. 5, where the coupling of the SS_e and Z_n reservoirs is shown schematically in the form of a thermal contact between bodies having definite specific heats (the double, single, wavy, and dashed arrows denote, respectively, direct thermal contact, the results of saturation of "forbidden" transitions, coupling with the lattice, and the additional channel of nuclear spin-lattice relaxation; the times of the corresponding processes are marked on the arrows).

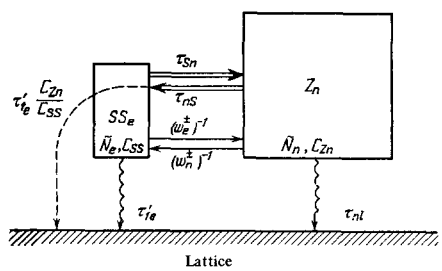

FIG. 5. Scheme of contact between the systems SS_e and Z_n.

From the stationary solution of (15) in the case of strong saturation of the "allowed" ESR transition it follows[25] that the condition for the equalization of the temperatures T_{Zn} and T_{SS} is satisfaction of at least one of the inequalities

$$\tau_{nS} \ll \tau_{nl}, \tag{16}$$

$$(w_n^{\pm})^{-1} \ll \tau_{nl}. \tag{17}$$

The conditions (16) and (17) have a very simple physical meaning and follow directly from an examination of the scheme of the thermal contact (see Fig. 5). If τ_{nl} is determined by "forbidden" electron-nuclear transitions accompanying the spin-lattice relaxation of the paramagnetic impurities[46], and is described by the same token by an expression similar to (14) but with a τ_{2e} replaced by τ_{1e}, then the condition (16) becomes

$$a\tau_{2e}\,[1 + (2\pi\nu_n a\tau_{2e})^{-2}] \ll \tau_{1e} \tag{18}$$

(we neglect here the difference between the averaged $\overline{\delta H}$ in the calculations of τ_{nS} and τ_{nl}[47], which is insignificant at low temperatures; in addition, we put $\tau_{1e}\nu_n \gg 1$). It follows from the same equations (15) that if

$$C_{SS}/C_{Zn} \gg \tau'_{1e}/\tau_{nl} \tag{19}$$

then the nuclear spins of the lattice do not influence the stationary value of T_{SS}, which is specified by the saturation of the ESR (formula (6)) or by the cross relaxation, and can therefore serve as a thermometer of sorts for the measurement of T_{SS}.

When the inequalities (16) and (19) are satisfied, the maximum enhancement of the nuclear polarization E, attainable in the "dynamic cooling" method and determined by relation (9), can be reached. Comparing this value with the maximum enhancement of the polarization in the "solid-state effect"[6,7], which is equal to ν_e/ν_n, we can conclude that the polarization of nuclei by contact with the SS_e reservoir may turn out to be, in principle, more effective than the "solid-state effect," provided only $2\gamma H_L\,(\tau_1/\tau_1')^{1/2} < \nu_n$[21]. However, owing to the random distribution of the paramagnetic centers, the quantity γH_L is usually quite large in comparison with τ_{2e}^{-1}, and it is apparently difficult to reconcile the last inequality with the condition (18) of good thermal contact.

The new DPN mechanism was investigated experimentally in[25] on ruby crystals (Al_2O_3) doped with Cr^{3+} ions. To exclude the possibility of the usual "solid-state effect," the ESR line was saturated in these experiments without a deviation from the center frequency, i.e., at exactly the frequency ν_e, and the T_{SS} shift was obtained as a result of cross relaxation between the different transitions of the ESR spectrum of ruby.

Figure 6 shows the experimental enhancement of the polarization E of[27] Al nuclei, obtained in the case of strictly resonant saturation of the 2–3 transition of the ESR spectrum (the energy levels of the Cr^{3+} ion are numbered upward), as a function of the angle θ between the field H_0 and the ruby axis[25]. The upper part of the figure is the diagram of the resonant frequencies of the ESR spectrum at ν_{23} = const (the dashed lines show the doubled frequencies; the arrows indicate the cross-relaxation regions). We see that in all the regions

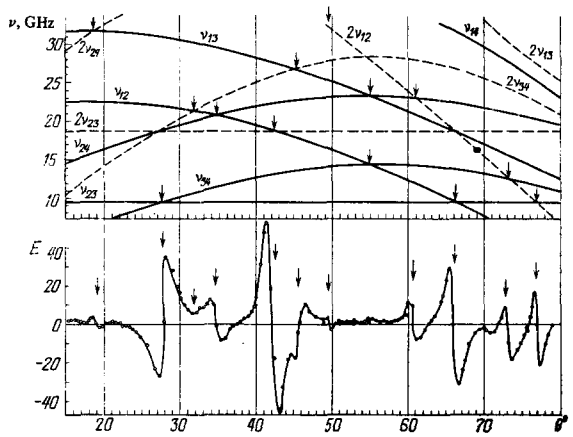

FIG. 6. Cross relaxation polarization of [27] Al nuclei in ruby under conditions of saturation of the center of the 2–3 transition of the ESR spectrum of Cr^{3+} (C = 0.3%, T_0 = 1.8°K.

where the frequencies of the different Cr^{3+} ion transitions (or their multiples) come close together, the nuclear polarization of[27] Al becomes enhanced, and the sign of E corresponds everywhere to the expected sign of T_{SS} (this effect can be called cross-relaxation nuclear polarization CRNP).

Estimates have shown[25] that inequalities (16) in (18) are satisfied under the conditions of these experiments, and consequently one should expect equalization of the temperatures T_{SS} and T_{Zn}. This prediction of the theory was verified in a number of experiments[25], where the temperature T_{SS} was measured, in particular, by analyzing the shape of the ESR line obtained with a weak microwave signal under conditions of pulsed saturation of the line center. Since $T_{Ze}^{-1} = 0$ in this case, it is clear from (5) that the absorption signal should be antisymmetrical with respect to ν_e, as was indeed observed in the experiment (see Fig. 7, where the turning on of the saturating pulse at the instant of passage through the line center is shown on the left, and the absorption line shape, observed 10 msec during the return sweep of the magnetic field is shown on the right; the equiilibrium line is shown dashed). The temperature T_{SS} determined from the magnitude of this signal with the aid of (5) turned out to be practically equal to T_{Zn} as measured directly from the NMR signal[27] of Al. The same result was obtained in a number of experiments in which electronic cross relaxation was used to determine T_{SS} (see Chap. 5).

It should be noted that in all these experiments the microwave pulses did not saturate "forbidden" transitions at the frequencies $\nu_e \pm \nu_n$, and thus the equalization of T_{SS} and T_{Zn} was apparently due to the direct thermal contact mechanism.

Evidence of the existence of the DPN mechanism through equalization of the temperatures T_{Zn} and T_{SS} was obtained also for other paramagnetic crystals. Thus, in Tutton salt of zinc doped with Cu^{2+} ions at helium temperatures, an "anomalous" doubly-exponential establishment of the proton polarization was obtained in not-strictly-resonant saturation of the ESR of the copper ions.[29] This singularity, as it turned out, can be explained within the framework of (15) if equalization of T_{Zn} and T_{SS} as a result of saturation of the "forbidden" transitions is assumed.

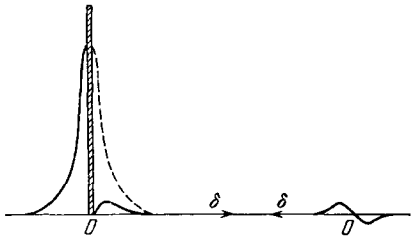

FIG. 7. ESR line shape of Cr^{3+} ion in ruby under the conditions of polarization of the nuclei ^{27}Al(E = 25, T_0 = 1.8°K).

A distortion of the ESR line shape, due to the antisymmetrical term in (5), was observed[30] in experiments on lanthanum-magnesium nitrate crystals with 2% Nd^{3+} ions under conditions of increased proton polarization at H_0 = 2.5 kOe and T_0 = 1.5°K. When the microwave field producing the DPN was turned off, this distortion vanished within the nuclear spin-lattice relaxation time τ_{1n}, i.e., in synchronism with the return of the Z_n system to equilibrium with the lattice. Although no quantitative comparison of the temperatures T_{SS} and T_{Zn} is reported in[30], this result undoubtedly favors the mechanism of the direct thermal contact of SS_e with Z_n; it is important that the contact exists in this case in the absence of any saturating microwave field.

The mechanism of "dynamic cooling" of the nuclear spins apparently plays an important role also in many other experiments on DPN[52,53], where appreciable deviations from the traditional "solid-state effect" picture are frequently observed. We note that the possibility of nuclear polarization in electronic cross relaxation was considered already in[52]. At that time, however, the concept of the spin-spin temperature had not yet suitably been developed, and the authors of these papers could not take correct account of the change in the energy of the spin-spin interactions, and therefore confined themselves only to an analysis of the special case $|\nu_\alpha - \nu_\beta| = \nu_n$.

The direct thermal contact between the Z_n and SS_e systems creates also an additional channel for spin-lattice relaxation of the nuclei. If $T_{Zn} \neq T_0$ at the initial instant of time (e.g., if the nuclei are polarized beforehand or are saturated by a high-frequency field), then the electronic SS reservoir, which is much more strongly coupled to the lattice than the Z_n system ($\tau'_{1e} \sim \tau_{1e} \ll \tau_{nl}$), turns out to be the intermediary between the nuclear spins and the lattice. Two limiting cases are possible here. If the "bottleneck" of the relaxation through the $Z_n \rightarrow SS_e \rightarrow$ lattice channel is the section $Z_n \rightarrow SS_e$, i.e., if $\tau'_{1e} \ll \tau_{Sn}$ (see Fig. 5), then the SS_e reservoir hardly deviates from equilibrium with the lattice during the relaxation process. In this case, obviously, this mechanism results in a nuclear spin-lattice relaxation time $\tau_{nSl} \approx \tau_{nS}$.

To the contrary, when $\tau'_{1e} \ll \tau_{Sn}$, the "bottleneck" of the relaxation process lines in the section $SS_e \rightarrow$ lattice, and the temperature T_{SS} is close to T_{Zn} at all times. As can be readily seen from an elementary analysis of the transient processes in the case of ther thermal contact between several bodies (see Fig. 5), we have here

$$\tau_{nSl} = [(C_{Zn} + C_{SS})/C_{SS}]\tau'_{1e} \approx (C_{Zn}/C_{SS})\,\tau'_{1e} \qquad (20)$$

(the second equality is the consequence of the relation $C_{Zn} \gg C_{SS}$, which usually holds for dilute paramagnets). The same expressions for τ_{nSl} are obtained rigorously from (15) by omitting from the latter the terms that take into account the action of the microwave fields[45].

It is obvious that the role of the SS_e reservoir in the spin-lattice relaxation of the nuclei will be decisive if

$$\tau_{nSl} \ll \tau_{nl}. \qquad (21)$$

If τ_{nl} is determined by the "traditional" mechanism of nuclear relaxation, due to the spin-lattice relaxation of the paramagnetic impurities of[46], then we can conclude, taking (14) into account, that in the case when the "bottleneck" occurs in the section $Z_n \rightarrow SS_e$, the inequality (21) reduces in practice to the requirement $\tau_{2e} \ll \tau_{1e}$, and is usually satisfied with a large margin; on the other, if the "bottleneck" is the section $SS_e \rightarrow$ lattice, then the influence of the SS_e reservoir on the spin-lattice relaxation of the nuclei will be significant only at not too small a ratio C_{SS}/C_{Zn}.

The possibility of spin-lattice relaxation of the nuclei via the SS_e reservoir was discussed theoretically quite long ago[54], but experiments that identify this relaxation mechanism uniquely were performed only in 1968, also on ruby crystals[25]. The time τ_{1n} of the[27] Al nuclei measured in[27] at liquid-helium temperatures in fields 1000—4000 Oe turns out to be shorter by three orders of magnitude than the time obtained by calculation on the basis of the "traditional" mechanism[46,47], but agrees well, on the other hand, with formula (20) (the ratio C_{Zn}/C_{SS} turns out to be here of the order of 10^2). The existence of a "bottleneck" in section $SS_e \rightarrow$ lattice was confirmed in this case also by an estimate of the values of τ_{nS} and τ_{nl}.

The "bottleneck" in the second section of the relaxation time through the channel $Z_n \rightarrow SS_e \rightarrow$ lattice was observed also in lanthanum-magnesium nitrate doped with Nd^{3+}, where the relation $\tau_{1n} \propto C_{SS}$ was noted[34], in yttrium ethyl sulfate doped with Dy^{3+} (see[55]), and in other substances.

Let us discuss also an interesting consequence of the thermal contact between the SS_e and Z_n systems, namely the thermal mixing of nuclear spins having different frequencies $\nu'_n \neq \nu''_n$, which lie, however, in the band $\sim \tau_{2e}^{-1}$. It is obvious that if each of the nuclear Zeeman systems Z'_n and Z''_n is effectively coupled with the SS_e reservoir, then the Zeeman temperatures T'_{Zn} and T''_{Zn} become equalized. In particular, saturation of one of the nuclear systems (say Z'_n) by a resonant field at frequency ν'_n will be transferred via the SS_e system to the second nuclear system (Z''_n), a fact observable by the double NMR method.

The influence of saturation of nuclear spins of one type on the NMR signal of nuclei of another type was observed in experiments[56] performed even prior to the development of the T_{SS} concept (these experiments pertained to the transfer of saturation from nuclear spins of the paramagnetic centers themselves to the lattice nuclei). Naturally, the authors of these papers could not interpret this phenomenon satisfactorily and confined themselves to vague references to "spin diffusion."

The idea of attributing these results to the thermal mixing via an SS_e reservoir was advanced in[24] and

was verified on Al_2O_3 crystals[27], the "different" nuclear spins employed here being five transitions of the NMR spectrum of[27] Al, separated by quadrupole splitting. In a crystal containing 0.03% Cr^{3+} ions, transfer of saturation (thermal mixing) was observed between these transitions at 1.9°K, whereas in a control experiment with pure Al_2O_3 there was no such transfer. The conditions of effective thermal mixing can be easily obtained from a scheme of the type of Fig. 5 and from the rate equations for T'_{Zn}, T''_{Zn}, and T_{SS}[27].

Thermal mixing of nuclear spins was recently observed also in a number of experiments[57-59] and was used, in particular, to increase appreciably the sensitivity of acoustic NMR (acoustic saturation of[53] Cr nuclei was revealed by the change of the NMR signal of[27] Al nuclei)[58]. We note also the possibility of establishing a single spin temperature T_{Zn} by thermal mixing of nuclear spins separated by a "diffusion barrier," i.e., situated in essentially different local fields produced by the paramagnetic centers. Apparently, thermal contact of these nuclei with the SS_e reservoir has a considerable effect on the phenomenon of "remote" electron nuclear double resonance (ENDOR), which consists of the transfer of saturation from the bulk of the lattice nuclei to the nearest paramagnetic-center neighbors that determine the ESR line shape[56,60].

5. NEW ASPECTS OF CROSS RELAXATION

It was already indicated in Chap. 2 that if two spin systems α and β having frequencies $\nu_\alpha \approx \nu_\beta$ (or $m\nu_\alpha \approx n\nu_\beta$) are present in a crystal, an important role is played by the interaction of Z_α and Z_β with the common SS reservoir (cross relaxation)[4]. Since the frequencies of these three subsystems are different, the energy balance occurring during their interaction calls for simultaneous changes in the population differences in all three reservoirs (e.g., n spins "α" go over to the lower Zeeman level, n spins "β" to the upper level, and n batches of energy $h\Delta_{\alpha\beta} \equiv h\nu_\beta - h\nu_\alpha$ are transferred to the SS reservoir). Dynamic equilibrium in the entire system as a whole sets in therefore when the algebraic sum of all three Boltzmann factors[2], the "stimulator" of the cross relaxation, becomes equal to zero:

$$\sigma_{\alpha\beta} \equiv (\nu_\beta/T_{Z\beta}) - (\nu_\alpha/T_{Z\alpha}) - (\Delta_{\alpha\beta}/T_{SS}) = 0. \qquad (22)$$

Generally speaking, the three temperatures $T_{Z\alpha}$, $T_{Z\beta}$, and T_{SS} can be different[9,22], and under conditions of a strong shift of T_{SS} the relation (22) does not mean at all an equalization of the Zeeman temperatures $T_{Z\alpha}$ and $T_{Z\beta}$ as predicted by the "traditional" theory[4].

Here and later on (Chap. 6) we shall refer to a cross relaxation as "effective" if it prevails over the spin-lattice relaxation, i.e., if

$$\tau_{cr} \ll \tau_1, \tau'_1. \qquad (23)$$

The rate equations for the temperatures in the general case of cross relaxation between many lines are written out in Chap. 6; we present here their solution for the case of two lines, α and β. If (23) is satisfied and the line α is strongly saturated exactly at the center, we have in the stationary regime[22]

$$1/T_{Z\beta} = (\Delta_{\alpha\beta}/\nu_\beta)/T_{SS} = 1/T_0[1 + (\Delta_0^{cr}/\Delta_{\alpha\beta})^2] \qquad (24)$$

where Δ_0^{CR} is defined in (10). It is seen from (24) that the saturation of the line α does not lead to a vanishing of $T_{Z\beta}^{-1}$, which is proportional to the absorption coefficient at the frequency ν_β. Moreover, according to (24), when $|\Delta_{\alpha\beta}| > \Delta_0^{CR}$ the transfer of the saturation from the spins α to the spins β can be negligible ($T_0/T_{Z\beta} > 1/2$), and the only essential result of the effective cross relaxation will in this case be an increase of $|T_0/T_{SS}|$. It is important that the condition (23) which is necessary for this purpose can be satisfied even for very large detunings $\Delta_{\alpha\beta}$, provided only the temperature T_0 is low enough.

We note that if the increase of $|T_{SS}^{-1}|$ is due to another factor acting simultaneously with the cross relaxation (e.g., to saturation of the line α at the frequency $\nu_\alpha + \Delta$), the line β may turn out to be not only "incompletely saturated" but even "cooled" ($T_0/T_{Z\beta} > 1$)[61] or inverted, depending on the relative signs of Δ and $\Delta_{\alpha\beta}$.

The theoretical prediction that the shift of T_{SS} limits the transfer of saturation over the ESR spectrum was first experimentally confirmed for ruby[24]. A study of the restoration of the ESR signal of the Cr^{3+} ions after pulsed saturation under cross-relaxation conditions has revealed a non-exponential section proportional to $t^{-1/2}$. Since such a dependence is characteristic of nuclear spin diffusion[47], the result was attributed to relaxation of the SS_e reservoir, greatly deviating from equilibrium with the lattice, to the Z_n system of the[27] Al nuclei. It is precisely this process which apparently limits here the rate of temperature equalization of the transitions involved in the cross relaxation.

More direct proof was obtained (likewise in ruby) in the already cited studies[25]. Thus, Fig. 6, which demonstrates the cross-relaxation nuclear-polarization (CRNP) effect, not only indicates a direct thermal contact between the Z_n and SS_e reservoirs, but also confirms the occurrence of a strong shift of T_{SS} in cross relaxation. The connection between this shift and the transfer of the saturation over the ESR spectrum was specially investigated in[25], with the transitions 1—2 and 2—3 of the Cr^{3+} ion in ruby at T = 1.8°K as examples.

Figure 8 shows the dependence of T_0/T_Z (1—2) (determined by measuring the absorption coefficient in the transition 1—2) on the detuning $\Delta_{\alpha\beta} = \nu_{23} - \nu_{12}$ under conditions when the 2—3 line is saturated (curve I,

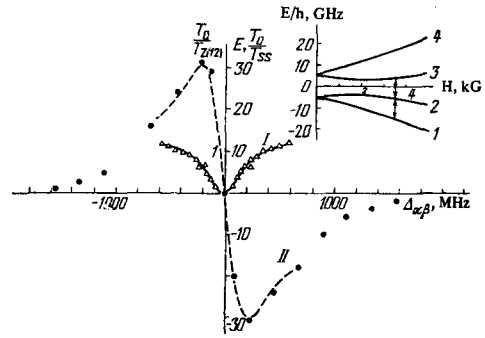

FIG. 8. Dependence of the reciprocal temperature of the 1—2 transition of the ESR spectrum of ruby on $\Delta_{\alpha\beta} = \nu_{23} - \nu_{12}$ under conditions of saturation of the 2—3 line.

left-hand scale; the top insert shows the energy level scheme of Cr^{3+} in ruby at $\theta = 66°$[25]); these data were used to calculate T_{SS} in accordance with[24], and the results were compared with the experimentally measured temperature T_{Zn} of the[27] Al nuclei (curve II, right-hand scale; dashed curve—the calculation of T_0/T_{SS} in accordance with formula (6), using curve I, points—experimental values of the enhancement of the polarization E of the[27] Al nuclei).

It is seen from Fig. 8 that in a wide range of detuning ($|\Delta_{\alpha\beta}| \leq 700$ MHz) the calculated values of T_{SS} agree well with the measured value of T_{Zn}, which is equal, owing to the direct contact between SS_e and Z_n (see Chap. 3), to the true temperature of the electronic SS reservoir. This means that the transfer of saturation is indeed limited in this case not by the increase of τ_{CR}, but by the shift of T_{SS}. We note that this shift, which leads to polarization of the nuclei, can serve as a rather sensitive indicator in the investigation of electronic cross relaxation.

Relation (22) can be used for deliberately altering the behavior and results of the cross relaxation by forcing a change in T_{SS}. Thus, saturation of the NMR signal of the lattice nuclei ($T_{Zn}^{-1} \to 0$) in the case of good contact between the Z_n and SS_e systems should lead to saturation (albeit partial) of the SS_e reservoir ($T_{SS}^{-1} \to 0$). It is obvious from (22) that in this case one should expect a stronger transfer of saturation over the ESR spectrum. This phenomenon, called "stimulated spectral diffusion" (SSD), was observed experimentally in ruby[25,32] and in barium fluoride doped with Er^{3+}[33]. It is shown in[32] that in the case of saturation of NMR of[27] Al in ruby, the SSD can increase the effectiveness of certain widely used quantum paramagnetic amplifier schemes in which the cross relaxation is used for simultaneous saturation of several pump transitions. We note that a similar effect was observed earlier[62], but was not explained there at all.

We indicate, finally, one more consequence of relation (22), namely the shortening of the time τ_{1n} of the nuclear spin-lattice relaxation under conditions of cross relaxation in the ESR spectrum of a paramagnetic impurity[24,25]. It was noted in Chap. 4 that in the case of relaxation of nuclei via the channel $Z_n \to SS_e \to$ lattice, the "bottleneck" of the process may turn out to be the second section, with $T_{SS} \approx T_{Zn}$ and $|T_0/T_{SS}| \gg 1$. Electronic cross relaxation connects, according to (22), the value of T_{SS} with the values of $T_{Z\alpha}$ and $T_{Z\beta}$. In the spin-lattice relaxation process, the temperatures $T_{Z\alpha}$ and $T_{Z\beta}$ tend to T_0, "dragging" T_{SS} with them, in accordance with (22). This produces an additional $SS_e \to$ lattice channel, which "widens" the "bottleneck" and decreases τ_{1n}.

This effect, which appears obviously only when $\Delta_{\alpha\beta} \neq 0$, can be regarded as the inverse of CRNP. It was observed in a number of studies (on ruby[63], on SrF_2 doped with Eu^{2+}[64] and on lanthanum magnesium nitrate doped with Nd^{3+}[65]), but the characteristic dependence of τ_{1n} on $\Delta_{\alpha\beta}$ was investigated only recently[25] (see Fig. 9, where 1 – C = 0.03%, $T_0 = 1.9°$K, 2 – C = 0.03%, $T_0 = 4.2°$K, 3 – C = 0.02%, $T_0 = 1.9°$K), and the appropriate calculation confirmed the interpretation proposed in[24].

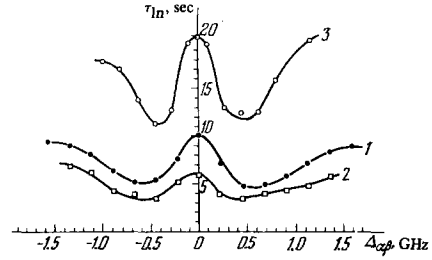

FIG. 9. Dependence of the spin-lattice relaxation time τ_{1n} of ^{27}Al nuclei in ruby on the frequency difference between the transitions 2–3 and 1–2 of the ESR spectrum of Cr^{3+} ($\theta = 66°$, $H_0 = 3400$ Oe).

6. CROSS RELAXATION IN A SYSTEM OF SPIN PACKETS AND THE PROBLEM OF INHOMOGENEOUS BROADENING

As already indicated (Chap. 2), the ESR lines in crystals are frequently inhomogeneously broadened (mainly because of the hyperfine structure and imperfections of the crystal), and it is therefore necessary to examine the behavior and the role of the SS reservoir in magnetic resonance with inhomogeneous broadening. In the theoretical investigations of this question the inhomogeneous line was traditionally[5,66] represented as consisting of homogeneous parts made up of groups of identical spins (spin packets). Initially the packets were assumed to be non-interacting and each was assigned its own spin-spin reservoir[67]. This corresponds, in particular, to a spatial separation of the packets (e.g., in the case of macroscopic inhomogeneity of the crystal or inhomogeneity of the external field); the characteristics of the magnetic resonance reduce in this case to a sum over independent packets, in which the possibility of variation of their T_{SS} is taken into account. However, in the typical case when the packets are spatially mixed, there are weighty arguments, both theoretical[68] and experimental[9,69], favoring the assumption that all the packets have a common SS reservoir; this was indeed assumed in the investigations which we now proceed to describe.

We denote the number of packets by m; then, on the basis of the theory of[1,2], the equations for the Zeeman temperatures T_i of each of them and for T_{SS}, with allowance for the probability w_{ij}^{CR} of the cross relaxation between packets i and j, for the spin-lattice relaxation, and for the action of the alternating field at the frequency ν, can be written in the form[70]

$$\left.\begin{aligned}
&\frac{d}{dt}\frac{\nu_i}{T_i} = -w_i\left(\frac{\nu_i}{T_i}+\frac{\nu-\nu_i}{T_{SS}}\right)+\sum_{j\neq i}^{m}\frac{\tilde{N}_j}{\tilde{N}_{ij}}w_{ij}^{KP}\sigma_{ij}\\
&\qquad -\frac{1}{\tau_1^{(i)}}\left(\frac{\nu_i}{T_i}-\frac{\nu_i}{T_0}\right), \quad i=1,\ \ldots,\ m,\\
&\frac{d}{dt}\frac{1}{T_{SS}} = -\sum_{i}^{m}\frac{\tilde{N}_i}{\tilde{N}}\frac{\nu-\nu_i}{(\gamma H_1)^2}w_i\left(\frac{\nu_i}{T_i}-\frac{\nu-\nu_i}{T_{SS}}\right)\\
&\qquad +\sum_{i<j}^{m}\frac{\tilde{N}_i\tilde{N}_j}{\tilde{N}_{ij}\cdot\tilde{N}}\frac{\Delta_{ij}}{(\gamma H_1)^2}w_{ij}^{CR}\sigma_{ij}-\frac{1}{\tau_1'}\left(\frac{1}{T_{SS}}-\frac{1}{T_0}\right);
\end{aligned}\right\} \qquad (25)$$

here ν_i is the frequency of the packet i, $w_i \equiv w_i(\nu - \nu_i)$ is the transition probability following action of a field of frequency ν on the packet i, σ_{ij} is defined in (22), $\tilde{N}_i = N_i \cdot S_i(S_i + 1)/3$, where N_i and S_i are the number and magnitude of the spins of the particles making up the

packet i, $\tilde{N}_{ij} = \tilde{N}_i + \tilde{N}_j$, $\tilde{N}$ is the sum of $\tilde{N}_i$ over all the particles having a common SS reservoir (obviously, there are $\geq m$ sorts of such particles), and $\gamma^2 = \sum \tilde{N}_i \gamma_i^2 / \tilde{N}$. We emphasize that Eqs. (25) pertain both to a single inhomogeneous line consisting of overlapping homogeneous sections, and to an aggregate of individual spectrally resolved lines with close frequencies; all that is required, obviously, is that the time τ_2 of formation of all the temperatures be much shorter than the time of the processes described by the system (25).

No general solution of Eqs. (25) was ever published, and only limiting cases were investigated in detail. Thus, from an examination of the stationary saturation of a system of non-interacting packets (when the cross relaxation between them* is not faster than the spin-lattice relaxation), it follows[68] that in the case of direct saturation of a small fraction of the spectrum, pertaining to the common SS reservoir, the growth of $|T_{SS}^{-1}|$ also turns out to be smaller in proportion; a similar result is obtained also when the effective cross relaxation involves a relatively small number of packets. Nonetheless the quantity $|T_0/T_{SS}|$ can still be appreciably larger than unity, as is manifest, for example, in the DPN effect[71], whereas the shape of the spectral dip in the ESR line should differ little from the traditional "hole burning" picture[66].

The manifestations of the SS reservoir are the most significant in a system of packets between which cross relaxation is effective (condition (23)); such a system is similar to a large degree to a system of identical spins. Indeed, as shown in[72], an analysis of Eqs. (25), abbreviated to cover "pure" cross relaxation, i.e., with only the terms σ_{ij} in the right-hand sides, makes it possible to separate from the total spin energy of all m packets two parts (high-frequency E_{HF} and low-frequency E_{LF}), which are the integrals of the motion in the cross-relaxation process and are transformed, as the result of the cross relaxation, into energies of two new reservoirs, each of which has a single temperature. Then the HF reservoir corresponds to one frequency ν_0 of the center of gravity of the system of m lines, and its specific heat is $C_{HF} = (h^2/k)\,\tilde{N}^{(m)}\nu_0^2$, where $\tilde{N}^{(m)} = \sum_i^m \tilde{N}_i$. The LF reservoir is produced by mixing of the spin-spin energy E_{SS} with a definite part E_Δ ("difference" part, connected with the difference Δ_{ij} between the frequencies of the packets) of the Zeeman energy of all the spins; its spectrum is quasi-continuous in a band $\sim \gamma H_{HL}$, Δ_{ij}, and the specific heat C_{LF} is the sum of the spin-spin specific heat $C_{SS} = (h^2/k)\,\tilde{N}(\gamma H_L)^2$ and the "difference" specific heat $C_\Delta = (h^2/k)\,\tilde{N}^{(m)} M_2$, where M_2 is the second central moment of the distribution of the spins over the packets.

The HF and LF reservoirs are the analogs of the reservoirs Z and SS, respectively, in the case of identical spins, the only difference being that the latter are produced more rapidly, within a time $\tau_2 \ll \tau_{CR}$. In analogy with the density matrix (3) for quasi-equilibrium over the spin-spin interactions of identical spins, we can now write down the density matrix $\hat{\rho}_{CR}$ for the quasi-equilibrium with respect to the cross-relaxation interactions

$$\rho_{CR} = \text{const} \cdot \exp\{[-\hat{\mathcal{H}}_{HF}/kT(\nu_0)] - [(\hat{\mathcal{H}}_\Delta + \hat{\mathcal{H}}_{SS})/kT_{SS}]\}. \quad (26)$$

Here $T(\nu_0)$ and T_{SS} are the temperatures of the HF and LF reservoirs, respectively, with Hamiltonians $\hat{\mathcal{H}}_{HF} = h\nu_0 \sum_i^m \hat{S}_{iZ}$ and $\hat{\mathcal{H}}_{LF} = \hat{\mathcal{H}}_\Delta + \hat{\mathcal{H}}_{SS}$, $\hat{\mathcal{H}}_\Delta = h\sum_i^m (\nu_i - \nu_0)\hat{S}_{iZ}$, and the subscript i denotes the number of the packet.

We note that an LF reservoir concept similar to that obtained above was introduced for the particular case of the hyperfine structure in[73], and the idea of quasi-equilibrium with a density matrix of the type (26) was advanced in[28].

It is clear from the foregoing that in systems with effective cross relaxation, if $\tau_1^{(i)} = \tau_1$, the spin-lattice relaxation should proceed in the same manner as in a system of identical spins, the relaxation rate of the HF reservoir being τ_1^{-1}, and that of the LF reservoir being a new quantity $\tau_1''^{-1}$, obtained by simple averaging over both its parts[72]: $\tau_1''^{-1} = (C_\Delta \tau_1^{-1} + C_{SS}\tau_1'^{-1})/C_{LF}$.

It is less clear how the idea of the HF and LF reservoirs is to be used under saturation conditions, when the action of the alternating field can be either slower or faster than the cross relaxation. However, an analysis of Eqs. (25), taken first without the spin-lattice terms and then taken in complete form, has shown[70,72] that strong saturation of at least one of the m lines is equivalent, under the condition (23), to a direct strong saturation of all m lines at the frequency ν, owing to their overlap. In both cases, the process reduces simply to thermal mixing of the energy of the SS reservoir with the Zeeman energies of all m packets in a coordinate system that rotates with a frequency ν, and with establishment of a single spin temperature $T_S^* = T_{SS}$[74], just as in the case of identical spins[17]. It follows therefore[72] that the result of the combined action of saturation in cross relaxation should not depend on the ratio of the rates of these processes and, in particular, will always be the same as in the case when the effective relaxation produces the HF and LF reservoirs even before the start of the saturation. This means that magnetic resonance in a system of packets connected by the condition (23) should be described (accurate to time intervals $\sim \tau_{CR}$) by the same formulas (5)–(9) as in the case of identical spins, with suitable changes of the parameters

$$(\gamma H_L)^2 \to (\tilde{N}/\tilde{N}^{(m)})(\gamma H_L)^2 + M_2, \quad \tau_1' \to \tau_1''. \quad (27)$$

Naturally, T_Z and T_{SS} must now be taken to mean the temperatures of the HF and LF reservoirs (it is shown in[72] that this conclusion is valid for an arbitrary degree of saturation). In particular, the shape of the signal $\mathcal{P}(\delta)$ for saturation at a frequency $\nu \neq \nu_0$ should be similar to that shown in Fig. 2: on one side of ν_0, beyond the saturation point, all the packets are inverted, and on the other side, starting with a definite frequency, the absorption exceeds the equilibrium value[70]. We can speak also of an analog of ADRF (see Chap. 2),

*We use the term "cross relaxation within the limits of an inhomogeneous line" in place of the traditional "spectral diffusion," for when account is taken of the SS reservoir the interaction between the packets is no longer described, generally speaking, by a diffusion equation of the type given in [5].

which gives the largest increase of $|T_{SS}^{-1}|$; now such an (isentropic) passage of the aggregate of lines under saturation conditions should terminate at the center of gravity ν_0 and should be slow in comparison with τ_{CR} (and obviously fast in comparison with τ_1 and τ_1'').

The idea of the equivalence (with respect to manifestations of the SS reservoir) of a group of lines coupled by effective cross relaxation to a single homogeneous line with spin-spin broadening was fully confirmed in a number of experiments. We have already noted that the experimental results considered in Chaps. 3—5, which were successfully interpreted with the aid of Provotorov's theory, were obtained for objects with an appreciable fraction of inhomogeneous broadening[23-25,27,31]. We might add that the data of[31] (see Figs. 3 and 4) are in good quantitative agreement with formulas (5) and (6) if the parameter (Δ_0^∞) in them is replaced, in accordance with (27), by the sum $(\Delta_0^\infty)^2 + M_2$ (at $\tilde{N}^{(m)} = \tilde{N}$). Even more convincing arguments were obtained in a study of groups of spectrally resolved ESR lines under cross-relaxation conditions[33,73]. Thus, in experiments on DPN and ENDOR in crystals of Tutton salt of zinc doped with Cu^{2+}[73], it was possible to describe the entire behavior of the four hfs lines of both copper isotopes in terms of two temperatures pertaining (in our notation) to the HF and LF reservoirs. In this case, the LF reservoir includes also the Zeeman system of the hydrogen nuclei, which enter in the crystal lattice and are in good thermal contact with the SS_e reservoir.

In[33], the model used for the spin packets forming the inhomogeneous line consisted of spectrally resolved ESR lines of the magnetically non-equivalent ER^{3+} ions in the BaF_2, which were coupled by cross relaxation. The form of this spectrum when one of the lines is saturated (Fig. 10) is quite similar to the shape of the homogeneous line in not strictly resonant saturation (see Fig. 2), with a characteristic induced radiation appearing on the saturated wing of the spectrum (beyond the saturation point). The thin line in Fig. 10 corresponds to equilibrium of the lattice, and the thick line corresponds to partial saturation of the central line (indicated by the arrow); the triangle shows the center of gravity of the spectrum; the line to the right is a superposition of two lines. It turned out that the absorption coefficients at the centers of all the lines practically coincided with the result of the calculation of $\mathcal{F}(\delta)$ for the homogeneous line in accordance with formula (5) (horizontal sections in Fig. 10) in which $g(\delta)$ was taken to be the form factor of the entire spectrum considered as a single line (the value of T_{SS} was determined by measuring the polarization of the[19] F nuclei, which assume here the role of the "thermometer"; see Chap. 4). The same experiments revealed the theoretically-predicted increase of the radiation on the "wing" of the spectrum when the saturation point is shifted to its center of gravity, and confirmed the need for making the substitution (27) in formula (7).

The foregoing results of the theoretical analysis of the behavior of an inhomogeneous line under the action of cross relaxation can be obtained also in another way, without resorting to the model of spin packets. This problem was solved in[26] on the basis of an equation for the density matrix, by introducing the concept of

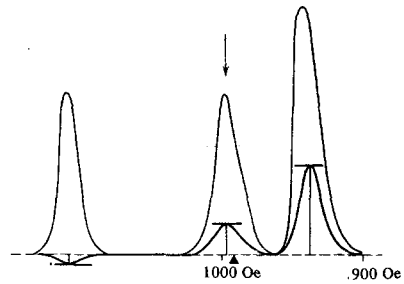

FIG. 10. ESR spectrum of Er^+ ion in BaF_2 under the conditions of saturation of one of the lines.

the "reservoir of local fields $\hat{L}$," which in essence coincides with the LF reservoir produced by cross relaxation between the packets. It is assumed that the spin-spin interactions establish in $\hat{L}$ quasi-equilibrium with one temperature after a time $\tau_3 \geq \tau_2$, i.e., one actually postulates the state described by the density matrix ρ_{CR}. It turns out here, naturally, that under the conditions $H_1 \ll H_L$ of interest to us, it is possible to obtain from[26] the same results as with the packet model.

The approach used in[26] makes it possible to generalize the T_{SS} concept to include cases of practical importance, when the separation of the spin packets within the limits of the inhomogeneous line is impossible, and particularly to include the case $\tau_{CR} \sim \tau_2$, which is intermediate between the case of a homogeneous line and the case of a set of packets coupled by effective cross relaxation (this is precisely the case realized apparently under the conditions of the experiments in[23-25,27,31]. Thus, in a system of spins that have either identical or close frequencies one can expect, regardless of the concrete energy exchange mechanism, the establishment of quasi-equilibrium over the spin-spin interactions, described by two temperatures. The behavior of such systems under magnetic-resonance conditions is the same, provided the spin-spin interactions are effective (are stronger than the spin-lattice interactions) and the alternating fields make no contribution to the specific heat of the spin system (for which purpose, undoubtedly, the condition $H_1 \ll H_L$ is sufficient). The difference between the homogeneous and inhomogeneous lines reduces only to a change in the time scale of the establishment of the quasi-equilibrium (τ_2 on the one hand, or τ_{CR} and τ_3 on the other).

We note in conclusion that the ESR lines are never fully homogeneous, even in the case of pure spin-spin broadening, owing to the random distribution of paramagnetic centers, which is characteristic of dilute electronic paramagnets. This is reflected, in particular, in the relation $\gamma H_L \gg \tau_2^{-1}$ that customarily holds for ESR[36] (in contrast to NMR, where $\gamma H_L \sim \tau_2^{-1}$; see Chaps. 3 and 4). An extreme manifestation of this is the appearance of additional lines in the ESR spectrum, due to the so-called "exchange pairs"[75]. The conclusion that the spin-spin temperature plays an important role in inhomogeneous line broadening acquires therefore a great importance for ESR in general.

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