Absorption of the energy of a low-frequency field by an electron spin-spin reservoir of transition ions in dielectric crystals

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Experiments on the optical detection of EPR in $CaF_2:Tm^{2+}$ and $Al_2O_3:Cr^{3+}$ have revealed the absorption of energy from a low-frequency alternating magnetic field orthogonal to the static magnetic field H_0 by the electron spin-spin reservoir of the transition ions. Possible mechanisms for absorption of the low-frequency field are discussed on the basis of an analysis of the magnitude and frequency dependence of the effect. It is shown that the mechanism of absorption in "forbidden" transitions at low frequencies, which is known in theory but has never before been observed in EPR, is operative in $Al_2O_3:Cr^{3+}$. In $CaF_2:Tm^{2+}$ a cross-relaxation mechanism is active. A study of the effect in $CaF_2:Tm^{2+}$ has yielded the cooling coefficient of the electron spin-spin reservoir and the dependence of this coefficient on the detuning of the microwave pump from the extremum of the EPR line.

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§1. INTRODUCTION

Optical detection methods, unlike conventional methods, permit observation of the electron paramagnetic resonance (EPR) under conditions of high saturation of the EPR line, when effects due to the spin temperature and the dynamical polarization of the nuclei appear.[1,2] Under strong microwave pumping, the shape of the optically detected (OD) EPR line contains information on the cooling of the electron spin–spin reservoir (SSR) and of the nuclear Zeeman subsystem in thermal contact with it. The heating of the nuclear subsystem by a resonant alternating field causes a change in the shape of the OD EPR line and permits experimental detection of the electron–nuclear double resonance (ENDOR) signal at distant nuclei in the lattice. It is of interest to use the OD EPR method in a study of some direct influence on the SSR. An influence of this kind might be parallel modulation of the static magnetic field.[3,4] However, parallel modulation of the magnetic field leads to a shift of the hole "burned out" by the microwave pump in the inhomogeneous EPR line and, hence, gives rise to parasitic signals that mask the effects of the heating of the SSR in OD EPR.[5] In addition, the heating of the SSR in the presence of parallel modulation of the static magnetic field H_0 depends on both the power of the microwave pump in the region of the EPR line and the detuning of the pump frequency from the extremum of the EPR line.[3]

This paper describes an attempt to find a means of heating the SSR which is independent of the simultaneous action of a microwave field, such as applying an alternating low-frequency field H_2 (which we shall call the transverse-modulation field) orthogonal to H_0. It is known[6] that a system of interacting spins in a magnetic field should absorb not only at the Larmor frequency $\omega_0 = \gamma_1 H_0$, where γ_1 is the gyromagnetic ratio, but also at forbidden transitions at low frequencies (of the order of the EPR linewidth) and at the multiple frequencies $2\omega_0$ and $3\omega_0$. Absorption at low frequencies is somewhat different from absorption by the SSR. This weak absorption is practically impossible to observe directly, but it can be observed indirectly by double-resonance methods. In nuclear magnetic resonance the absorption of a low-frequency field by the spin-spin reservoir of ^7Li nuclei in metallic lithium was observed in nuclear magnetic resonance by Anderson and Hartman[7] using the method of "adiabatic demagnetization in a rotating coordinate system." To the best of the author's knowledge, absorption at low frequencies at the forbidden transitions has not previously been observed in EPR.

This paper describes the heating of the SSR of the electron spins of Tm^{2+} in CaF_2 and of Cr^{3+} in Al_2O_3 under the action of a low-frequency transverse-modulation field. The effect was observed through the OD EPR spectra of these transition ions under a microwave pump which saturated the EPR. Some of the results presented here were briefly described[1)] in an earlier note.[5]

§2. EXPERIMENTAL OBJECTS, TECHNIQUES, AND RESULTS

Optical detection by magnetic circular dichroism in the absorption bands has been used to study the EPR spectra of the Tm^{2+} ion (with an isotropic g factor $g = 3.454$) in CaF_2 and fo Cr^{3+} in Al_2O_3. The samples and the optical detection techniques were the same as those used earlier.[1,2] The frequency and intensity of the microwave pump at which the EPR was detected were $\nu_1 = 8.91$ GHz and $H_1{}^2 \lesssim G^2$.

A CaF_2 sample containing Tm^{2+} ions (the effective spin of the electron shell of Tm^{2+} is $S = 1/2$; the nuclear spin of ^{169}Tm is $I = 1/2$) at a concentration $n_0 \sim 10^{18}$ cm^{-3} (see Table I) was studied in the region of the high-field EPR line ($H_0{}^{max} = 1950$ G) of the Tm^{2+} ion for a crystal orientation of $\mathbf{H}_0 \| C_3$. The change ΔS_e of the line shape S_e of the OD EPR line upon application of the transverse low-frequency field on was studied for various intensities of the microwave pump. Figures 1(a) and (c) show the OD EPR line shapes in the absence and presence of transverse modulation of the static magnetic field.

For studying the change $\Delta S_e = S_e(H_2) - S_e(H_2 = 0)$ in the line shape at small amplitudes of H_2, a modulation tech-

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TABLE I. Parameters of the investigated $CaF_2:Tm^{2+}$ samples and summary of the experimental data

	Samples	
	№ 1	№ 2
$n_0(Tm^{2+})$, cm^{-3}	$1\cdot10^{18}$	$2.4\cdot10^{18}$
T_2^{-1}, cm^{-1}	$2.8\cdot10^{8}$	$4\cdot10^{8}$
τ_1, sec	$1\cdot10^{-1}$	$2\cdot10^{-3}$
τ_2, sec	$4\cdot10^{-7}$	10^{-7}
R	0.09 *	0.17 *
$a\omega_{SS}^2$, sec^{-2}	$(6\pm1)\cdot10^{17}$	$(1.2\pm0.2)\cdot10^{18}$
$a\omega_{SS}^2+\int(\omega'-\Omega)^2FGd\omega'$, sec^{-2}	$(7.3\pm0.7)\cdot10^{17}$	$(1.75\pm0.15)\cdot10^{18}$
(β_{SS}^{M}/β_L)	21 ± 2 *	18 ± 2 *
$(\beta_{SS}^{M}/\beta_L)_{hom}$	16 *	15.6 *

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*At $H_1^2=0.6$ G^2

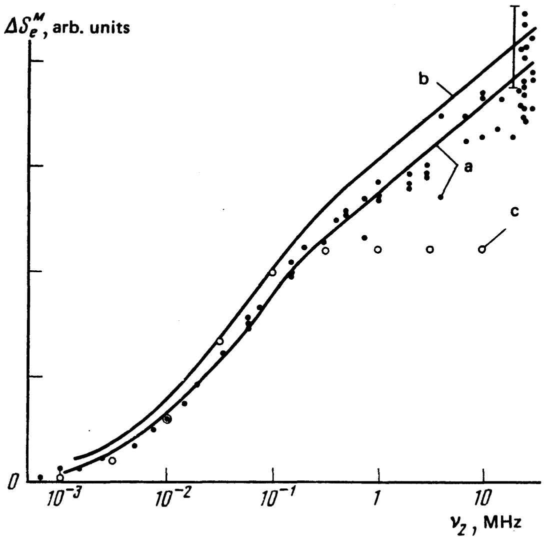

FIG. 2. The experimental dependence of ΔS_e^M on the frequency ν_2 of a transverse modulation field of amplitude H_2 = 1 G for CaF_2:Tm sample No. 1 (a) and No. 2 (b). c) The calculated dependence for a cross-relaxation mechanism (see text). The scale of the abscissa is logarithmic; the scale on the ordinate, linear.

nique was used to detect the signals. In this case the amplitude of the low-frequency field H_2 was meander-modulated at frequencies of ν^{mod} = 0.4 and 17 Hz$\ll\tau_1^{-1}$, where τ_1 is the longitudinal relaxation time of Tm^{2+} in the samples (see Table I). Figure 1c shows the resulting change in the line shape of $CaF_2:Tm^{2+}$. Figures 2a and b show the behavior of ΔS_e^M (the maximum of ΔS_e in the region of the OD EPR line at the optimum detuning; see below) as a function of the frequency ν_2 of the low-frequency field at a constant amplitude H_2 = 1 G for the samples studied. The field strength H_2 in the sample was determined from the voltage induced by the low-frequency field in a thin wire loop around the sample. Figures 3a and b show ΔS_e^M as a function of the amplitude H_2 of the low-frequency field. One notices that the function $\Delta S_e(H_0 - H_0^{max})$ changes noticeably when a second low-frequency field $\mathbf{H}_2^{(2)}\perp\mathbf{H}_0$, which is not amplitude modulated, is applied (Fig. 1d). The relative size $\Delta(\Delta S_e)/\Delta S_e$ of this change (for small H_2) is important for certain estimates (see below) and was expressly determined.

The signals ΔS_e were not found to depend in any way on the orientation of the samples in the interval $\theta\leqslant10°$, where θ is the angle between $\mathbf{H}_0$ and $\mathbf{C}_3$. The dependence of ΔS_e^M on the size of the microwave field in the resonator was studied;

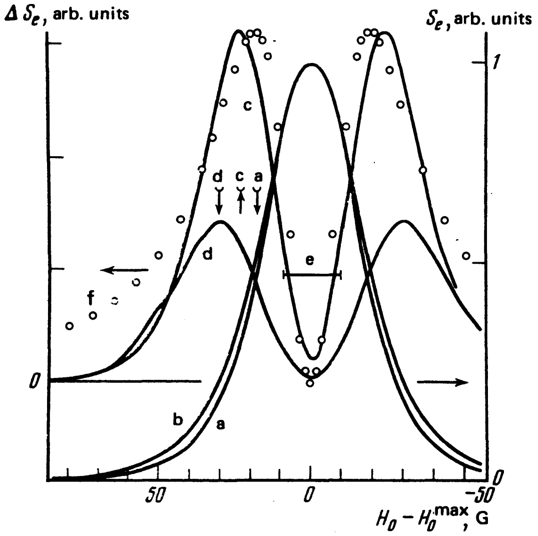

FIG. 1. a) Optically detected EPR line shape S_e at a microwave field H_1^2 = 0.6 G^2 in $CaF_2:Tm^{2+}$ sample No. 1; c) the change ΔS_e in the OD EPR line shape upon application of a weak transverse field at ν_2 = 3.8 MHz; b,d) the same as a,c) but with the simultaneous action of a strong transverse field H_2 = 3.5 G at ν_2 = 0.27 MHz. The arrows indicate the peaks of the curves c and d and the half-width of line a. The length of segment e corresponds to the width of the EPR line for $H_1^2\to0$. f) the calculated dependence of ΔS_e (the points; see text).

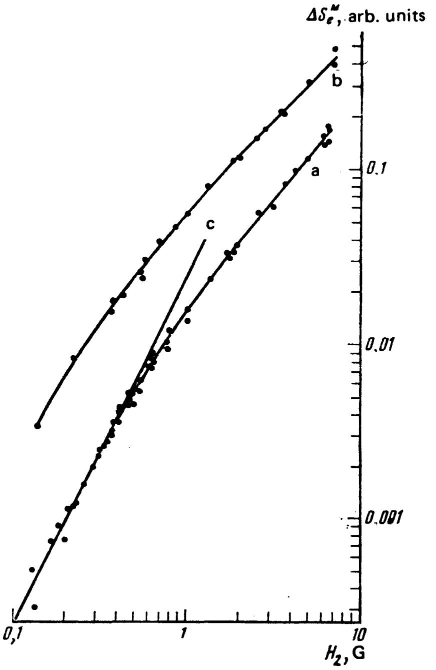

FIG. 3. The experimental dependence of ΔS_e^M on the amplitude H_2 of the transver low-frequency (ν_2 = 10 MHz) field in CaF_2:Tm samples No. 1 (a) and No. 2 (b). c) The approximation $\Delta S_e^M\propto H_2^2$.

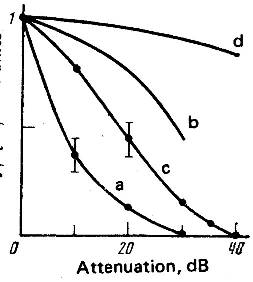

FIG. 4. The experimental behavior of ΔS_e^M (curves a,c) and of the line intensity $S_e^{\max}$ (curves b,d) as functions of the attenuation of the microwave field in the resonator. At an attenuation of 0 dB the field is $H_1^2 = 1\ \mathrm{G}^2$. a,b) CaF_2:Tm sample No. 1; c,d) No. 2.

it is compared with the dependence of the line intensity $S_e^{\max}$ on the microwave field in Fig. 4.

In $Al_2O_3:Cr^{3+}$ the measurements were made in a field $H_0 \simeq 3.2$ kG at an orientation $\mathbf{H}_0 \| \mathbf{C}$ (the angle between $\mathbf{H}_0$ and $\mathbf{C}$ was less than 1°). The chromium content of the sample was 0.02 mol.%. A study was made of the change ΔS_e in the OD EPR signal at the transition $-1/2 \rightarrow +1/2$ upon application of the low-frequency transverse magnetic field. It was found that the transverse modulation of the static magnetic field led to broadening of the OD EPR line of the Cr^{3+} ion, without changing the amplitude of the line. The change in the line shape when the transverse low-frequency field was turned on was of the same form as that found in recording the spectrum of the optically detected ENDOR (see Fig. 2 in Ref. 1) and is not shown here. The dependence of ΔS_e^M on the frequency of the low-frequency field, scaled to a field amplitude $H_2 = 1$ G, is shown in Fig. 5. This dependence was not studied in detail in the interval 1–10 MHz, in which there are strong lines of the optically detectable ENDOR spectrum of distant ^{27}Al nuclei.

§3. DISCUSSION OF THE EXPERIMENTAL RESULTS FOR $CaF_2:Tm^{2+}$

3.1 Determination of the temperature of the electron SSR

One can explain the experimental results by assuming that the transverse modulation of the static magnetic field leads to a heating of the electron SSR. At the high intensities of the microwave pump that were used in the recording of the OD EPR spectrum, the linewidth is directly related to the temperature of the SSR,[2] so that the heating of the SSR should lead to broadening of the OD EPR line. At the same time, the amplitude of the OD EPR signal at the center of the line is independent of the state of the SSR, so it is not surprising that at $H_0 = H_0^{\max}$ the turning on of the transverse modulation does not have an observable effect. It is to be expected on the basis of Refs. 1 and 2 that the most noticeable deformation of the OD EPR line shape under the influence of agencies which heat the SSR should be observed when the microwave pump is such that the intensity of the OD EPR line is close to saturation: $S_e^{\max} \rightarrow 1$, whereupon ΔS_e should grow monotonically with the square of the microwave field amplitude H_1^2. Such a behavior is in fact displayed by $\Delta S_e^M(H_1^2)$ in the investigated samples (see Fig. 4). The dependence of ΔS_e^M on the amplitude H_2 of the low-frequency transverse field (for small H_2) is of the form $\Delta S_e^M \propto H_2^2$ (see Fig. 3), indicating the presence of absorption of the transverse low-frequency field by the spin system.

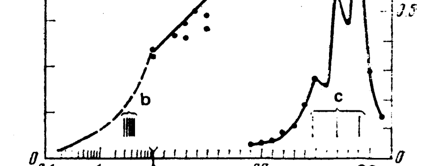

FIG. 5. The experimental values (points) of ΔS_e^M for $Al_2O_3:Cr^{3+}$ as a function of the frequency ν_2 of the transverse modulation field at an amplitude $H_1^2 = 1\ \mathrm{G}^2$. The static magnetic field is $H_0 = 3.26\ \mathrm{kG}^2$. a) The calculated linear dependence $\Delta S_e^M \propto \nu_2$. The frequencies of the NMR spectrum of the ^{27}Al lattice nuclei (b) and of the ^{53}Cr nuclei (c) are indicated by hash marks; $\theta \simeq 0.8°$; for $^{53}Cr^{3+}$ we have $S_z = 1/2$.

Let us examine the effects on the optical detection of EPR when the SSR is heated. We assume, as usual,[2] that in this case $|\beta_{SS}| \gg \beta_L$ (β_{SS} and β_l are the reciprocal temperatures of the SSR and lattice). Further, we do not take into account the leakage of cooling of the SSR through the nuclear subsystem,[8] assuming that this leakage is inconsequential. The relaxation of β_{SS} under conditions in which the SSR is heated is described by the equation[8]

$$\left(\frac{d\beta_{SS}}{dt}\right)_{rel} = -\frac{\beta_{SS}-\beta_L}{\tau_{SSL}} - \frac{\beta_{SS}}{\tau_{SSO}} \approx -\beta_{SS}(\tau_{SSL}^{-1}+\tau_{SSO}^{-1})$$
$$= -\beta_{SS}(w+\Delta w). \tag{1}$$

Here $\tau_{SSL}^{-1} = w$ is the spin-lattice relaxation rate of the SSR,and $\tau_{SSO}^{-1} = \Delta w$ is the rate of heating of the SSR by the external agency, in this case the low-frequency transverse field. Using the formulas of Ref. 2 for the optically detectable line shape of an inhomogeneous EPR line in the absence of spectral diffusion, we have (for $\Delta w \ll w$)

$$\Delta S_e(\Omega-\omega_0) = (\tau_1\omega_{SS}^2\Delta w/\omega_0^2)E_{SS}^2(\Omega-\omega_0). \tag{2}$$

Here $\Omega = 2\pi\nu_1$ is the frequency of the microwave pump, ω_{SS} is the average frequency of the SSR, and $E_{SS} = \beta_{SS}/\beta_L$ is the cooling coefficient of the SSR. We note that in our case Δw is determined solely by the applied transverse-modulation field and does not depend on the detuning $\Omega - \omega_0$. Therefore, the experimental dependence of ΔS_e on the magnetic field H_0 (Fig. 1c) reflects the behavior of E_{SS}^2 as a function of the detuning at a fixed intensity of the microwave pump, while ΔS_e^M as a function of the microwave pump H_1^2 (Figs. 4a and c) describes the dependence on H_1^2 of the square $(E_{SS}^M)^2$ of the maximum cooling coefficient of the SSR at the optimum detuning. We note that formula (2) is also valid for describing the ΔS_e effects for homogeneous and quasihomogeneous EPR lines, while in the limit of a high intensity of the microwave pump it also works for inhomogeneous lines having a narrow spectral diffusion (for $\sqrt{s}/\tau_2 > l_{CR}$, where $s = \frac{1}{4}\gamma_1^2 H_1^2 \tau_1 \tau_2$ is the saturation parameter, τ_2 is the transverse relaxation time of the spin packet in the inhomogeneous EPR line, and l_{CR} is the spectral diffusion length[8]).

Experiments were carried out to determine the absolute value of E_{SS}, using two independent low-amplitude fields H_2. A measurement was made of the relative change in ΔS_e upon application of the second field $H_2^{(2)}$:

$$\frac{\Delta_2(\Delta S_e)}{\Delta S_e}=2\frac{\Delta_2\beta_{SS}}{\beta_{SS}}$$

$$=2\tau_1\omega_{SS}^2\Delta_2 w\Big/\Big[a\omega_{SS}^2+\int(\omega'-\Omega)^2FGd\omega'\Big]=C_2. \tag{3}$$

Here $\Delta_2\beta_{SS}$ and $\Delta_2 w$ are the changes in the corresponding parameters upon application of the second field $H_2^{(2)}$, $a=\tau_1 w$ is a parameter, and $F=F(\omega'-\Omega,s)$ is the saturation function of the spin packets in an homogeneous EPR line of Gaussian shape $G=G(\omega'-\omega_0)$ and width $2T_2^{-1}$ (Ref. 2). If we also define the effect $\Delta S_e=A_2$ for the field $H_2^{(2)}$, we have

$$E_{SS}^2(\Omega-\omega_0)=R(\Omega-\omega_0)\,\omega_0^2\Big/\Big[a\omega_{SS}^2+\int(\omega'-\Omega)^2FGd\omega'\Big],$$

$$R(\Omega-\omega_0)=\frac{2A_2}{C_2}. \tag{4}$$

To achieve the highest experimental accuracy, the measurements were made at the optimum detuning, which, as was shown in Ref. 2 and is confirmed in the experiment (see below), is approximately equal to the half-width of the OD EPR line and varies with the microwave pump. The unknown quantity—the denominator in the expression for E_{SS}^2 in (4)—can be determined at the optimum detuning by analyzing how the optically detected linewidth depends on the microwave pump.[2] The values thus obtained for this denominator were used to find E_{SS}^M from formula (4), which, in turn, yielded a refined value of the parameter $a\,\omega_{SS}^2$ (see Table I). We note that the accuracy with which E_{SS}^M can be determined in this way is rather high ($\pm 10\%$), with the result depending only weakly on the assumptions about the shape of the spin packets.

Interestingly, in the model of Ref. 8 for a homogeneous or quasihomogeneous EPR line (and for any model when the intensity of the microwave pump $s\rightarrow\infty$), the ratio R at the optimum detuning, which corresponds to the half-width $\Delta_{1/2}$ of the OD EPR line, uniquely determines the cooling of the SSR:

$$(E_{SS}^M)^2_{\text{hom}}=\frac{4R^2}{(1+2R)^2}\frac{\omega_0^2}{\Delta_{1/2}^2},\quad a\omega_{SS}^2+(2T_2^2\ln 2)^{-1}=\Delta_{1/2}^2\,\frac{1+2R}{4R}. \tag{5}$$

Estimates of E_{SS}^M under the crude assumption of a quasihomogeneous EPR line for the CaF_2:Tm^{2+} samples studied give, as expected, only slightly underestimated values of E_{SS}^M (see Table I).

In Figs. 1c and f the experimental $\Delta S_e(H_0-H_0^{\max})$ dependence is compared with the dependence calculated from formula (2), using relation (5) of Ref. 2, for several typical values of the parameters (see the table in Ref. 2). It is seen that there is generally satisfactory agreement between theory and experiment, although some discrepancies do exist. First, the experimental peaks in $\Delta S_e(H_0-H_0^{\max})$ are shifted to somewhat larger detunings from those of the experimental curve; second, as the detuning is increased to $\simeq$80 G, one observes an unexpected sharp drop in ΔS_e, almost to zero.

The first of these anomalies is possibly due to a heating of the SSR during the recording of the ΔS_e signal (see below), and the second to a more rapid falloff of the far wings of the EPR line than is given by the uncutoff Lorentzian curve adopted in the calculation. To check this latter assumption, the shape of the OD EPR line was recorded at very large detunings. It turned out that the wings of the EPR line in sample No. 2 agree with the theoretically predicted shape of a dipole-broadened spin packet, which is a cutoff Lorentzian curve[8] with a cutoff parameter $\Delta H_0^{\text{cut}}\simeq 200$ G. This last quantity, in turn, agrees with the value $\tau_2\simeq 10^{-7}$ sec obtained by an independent method.[2] However, this value of ΔH_0^{cut} is nevertheless too large to explain the sharp drop in ΔS_e for $H_0-H_0^{\max}\geqslant 80$ G. This is even more true for sample No. 1, in which it was found by OD EPR that the wings of the line extend to 400 G.

It is possible that the disagreement can be explained by the presence of an additional peak on the wings of the OD EPR line (at $H_0\simeq 2.07$ kG), which could be ascribed to the strongly forbidden three-particle transition in the ensemble of Tm^{2+} spins: $(--)(++)(--)\rightarrow(+-)(-+)(++)$. The signs indicated here are those of the spin moments of the elecrtron shell and nucleus for the ^{169}Tm ions involved in the transition. We note that a somewhat stronger transition of this same type, $(+-)(-+)(--)\rightarrow(--)(++)(++)$, is observed in the OD EPR spectrum at $H_0=1.61$ kG. It is also possible that the reason for the disagreement between theory and experiment at large detunings lies in the nonuniform distribution of Tm^{2+} ions over the volume of the samples, which turns out to be more important for sample No. 1.

It is of interest to track the change in ΔS_e and in the line shape S_e during an additional strong heating of the SSR by a second, steady, low-frequency tranverse field. Such a heating can appear as a significant increase in the relaxation rate of the SSR: $\Delta_2 w\sim w$. As expected, a substantial change is observed here in ΔS_e (cf. curves c and d in Fig. 1): Its intensity decreases, and the distance between humps increases. The shape of the OD EPR line, on the other hand, changes insignificantly during such a heating of the SSR (Figs. 1a and b).

From the value of ΔS_e or $\Delta(\Delta S_e)/\Delta S_e$ in the viciity of the OD EPR line one can determine the experimental value of $\tau_1\omega_{SS}^2\Delta w$, which we shall later compare with the theoretical estimates of various models. For $H_2=1$ G and $\nu_2=30$ MHz we have $(\tau_1\omega_{SS}^2\Delta w)_{\exp}=1.3\times 10^{17}$ sec^{-2} and 6×10^{17} sec^{-2}, respectively, for samples No. 1 and 2.

3.2.a. Mechanism for the heating of the SSR: Absorption in forbidden transitions at low frequencies

The most natural mechanism for the heating of the SSR during transverse modulation of the static magnetic field is expected to be the absorption of energy from the modulation field by the ensemble of electron spins in forbidden transitions at low frequencies $\omega_2=2\pi\nu_2\ll\omega_0$ (see §1). The energy absorbed per unit time by the SSR from the transverse low-frequency field is given[2)] by the formula[7]

$$P^{(0)}=\frac{\pi}{8}\gamma_1^2H_2^2\frac{\hbar^2\omega_2^2}{2k}\beta_{SS}\frac{\omega_{SS}^2}{\omega_0^2}\left(\frac{2\ln 2}{\pi}\right)^{1/2}T_2$$
$$\times\exp\left[-\frac{\omega_2^2}{2}T_2^2\ln 2\right]n_0=\Phi_0\beta_{SS}. \qquad (6)$$

The value of ω_{SS}^2 can be found from the intensity of the satellite of the EPR line at frequency $2\omega_0$ (Ref. 6). The microwave power absorbed in the region of this satellite is

$$P^{(\omega\approx 2\omega_0)}=\frac{\pi}{12}\gamma_1^2H_1^2\frac{\omega_{SS}^2}{\omega_0^2}\frac{\hbar^2\omega^2}{2k}\beta_L\left(\frac{2\ln 2}{\pi}\right)^{1/2}T_2$$
$$\times\exp\left[-\frac{(\omega-2\omega_0)^2}{2}T_2^2\ln 2\right]n_0. \qquad (7)$$

The $2\omega_0$ satellite is easily observed in the optical detection method.[9] The measurements made in the present study by a technique analogous to that of Ref. 9 yielded an estimated value of $\omega_{SS}^2\sim 10^{16}$ sec^{-2} for the samples used.

We can now estimate the heating of the SSR by a transverse low-frequency field. The power absorbed by the SSR is

$$P^{(0)}=\Phi_0\beta_{SS}=c_{\text{SSR}}\frac{d\beta_{SS}}{dt},$$

where, in accordance with Ref. 8, $c_{\text{SSR}}=n_0\omega_{SS}^2\hbar^2/4k$ is the specific heat of the SSR for $S=1/2$. Hence,

$$\Delta w=\Phi_0/c_{\text{SSR}}=\frac{\pi}{4}\frac{H_2^2}{H_0^2}\omega_2^2\left(\frac{2\ln 2}{\pi}\right)^{1/2}T_2\exp\left[-\frac{\omega_2^2}{2}T_2^2\ln 2\right]. \qquad (9)$$

We note that Δw depends on the EPR linewidth as well as on the parameters of the low-frequency field. For $\text{CaF}_2:\text{Tm}^{2+}$ we have $\Delta w\sim 15$ sec^{-1} for $H_2=1$ G and $\nu_2=30$ MHz. Then $(\tau_1\omega_{SS}^2\Delta w)_{\text{theor}}=3\times 10^{14}$ and 1.5×10^{16} sec^{-2} for samples No. 1 and 2—values which are from one to three orders of magnitude lower than the experimental values. It must be pointed out that the mechanism under consideration should lead to a dependence $\Delta S_e^M\propto\nu_2^2$, which is not confirmed by experiment. The observed frequency dependence of S_e^M (see Figs. 2a and b) apparently corresponds to the cross-relaxation mechanism examined below.

3.2.b. Cross-relaxation mechanism for the heating of the SSR

If a crystal contains several spin systems which have a common SSR and are coupled with one another by cross relaxation, a state of dynamic equilibrium is established between the systems and the SSR (in either the presence or absence of microwave pumping) and can be disrupted by an outside influence. In particular, the change in the energy gap between the Zeeman sublevels of the interacting spins upon modulation of the magnetic field (modulation of the detuning) leads to a heating of the SSR.[3,4] The energy absorbed from the modulation field by the spins in a unit time is[3,10]

$$P_{CR}=\frac{1}{2}\frac{I(\omega)}{\tau_{CR}}\frac{\omega_{SS}^2}{\omega_{SS}^2+M_2}\frac{n_0}{4k}\beta_{SS}(\Delta\sqrt{M_2})^2=\Phi_{CR}\beta_{SS}, \qquad (10)$$

where

$$I(\omega)=\left(\frac{3}{2\pi}\right)^{1/2}\int\limits_0^{\tau_{CR}\omega_{\max}}y^{1/2}\frac{(\omega\tau_{CR})^2}{(\omega\tau_{CR})^2+y^2}e^{-3y/2}dy\approx\frac{(\omega\tau_{CR})^2}{1+(\omega\tau_{CR})^2},$$

τ_{CR} is the cross-relaxation time, $\omega_{\max}$ is some cutoff frequency ($\omega_{\max}\tau_{\text{CR}}\geqslant 1$), and $\Delta\sqrt{M_2}=(d\sqrt{M_2}/d\mathbf{H}_0)\Delta\mathbf{H}_0$ is the change in the normalized second moment of the envelope of the EPR spectrum of the interacting spins upon modulation of the amplitude ΔH_0 and frequency ω. The corresponding value of $\tau_1\omega_{SS}\Delta w$ (under the condition $\omega_{SS}^2>M_2$) is

$$(\tau_1\omega_{SS}^2\Delta w)_{CR}=\tau_1\omega_{SS}^2\frac{\Phi_{CR}}{c_{\text{SSR}}}=\frac{I(\omega)}{2\tau_{CR}}(\Delta\sqrt{M_2})^2\tau_1. \qquad (11)$$

The experimental frequency dependence of $\Delta S_e^M(\nu_2)$ is in satisfactory agreement with the calculated dependence for a cross-relaxation mechanism, $\Delta S_e(\nu_2)\propto I(\omega=2\pi\nu_2)$, at parameter values of $(2\pi\tau_{\text{CR}}^{-1}=1$ kHz, $\omega_{\max}\tau_{\text{CR}}=70$, and $I(\omega\to\infty)=10$ (see Fig. 2).

One of the possible causes of the change in M_2 when the static magnetic field is modulated, giving rise to cross relaxation, is a shift of the spin packets in the inhomogeneous EPR line as a result of the fact that the total hyperfine-interaction energy of the electron spin with the nuclear moments of the ligands depends on the strength and orientation of the external magnetic field.[11] It is easy to show, however, that in this case one has an order of magnitude $\Delta\sqrt{M_2}\sim\gamma_nH_2$, where γ_n is the nuclear gyromagnetic ratio, so that the size of the corresponding effect $(\tau_1\omega_{SS}^2\Delta w)_{\text{CR}}$ (see Ref. 11) is negligibly small.

It can be supposed that the observed heating of the electron SSR is due to the presence in the samples of an extraneous (other than Tm^{2+}) paramagnetic impurity, with cross relaxation possible between the electronic levels of this impurity or between the extraneous impurity and the Tm^{2+} ions. Following the usual prescription,[3,8] one can obtain an expression for the ratio of the concentration of the extraneous paramagnetic impurity $(\tilde{n}_s)$ to that of the microwave-active Tm^{2+} ions $(n_s=n_0/2)$ which would be required to explain the observed effect:

$$\tilde{n}_S/n_S=2\tau_{CR}(\tau_1\omega_{SS}^2\Delta w)_{\text{exp}}/I(\omega)\tau_1(\Delta\sqrt{M_2})^2,$$

from which, assuming that $\Delta\sqrt{M_2}\sim\gamma_eH_2\sim 10^7$ sec for the electronic cross relaxation, we find the values $\tilde{n}_s/n_s=5$ for sample No. 1 and $\tilde{n}_s/n_s=0.5$ for sample No. 2.

Thus, in order for the cross-relaxation mechanism to be realized in $\text{CaF}_2:\text{Tm}^{2+}$ it is necessary to have a significant concentration of an extraneous paramagnetic impurity. We note that the presence of an extraneous impurity in our samples (see also the table in Ref. 2) is indicated by the experimental estimate of the parameter $a\sim 100$, which is much greater than the theoretically predicted[8] value of three. Furthermore, a study of the OD EPR spectra in our $\text{CaF}_2:\text{Tm}$ samples in the absence of Tm^{2+} ions (prior to the partial reduction $\text{Tm}^{3+}\to\text{Tm}^{2+}$; see Ref. 2) has revealed a significant concentration of a paramagnetic impurity, which can apparently be identified as anisotropic Tm^{3+} centers with wide EPR lines. The cross-relaxation mechanism for the absorption of the transverse low-frequency field by the electron SSR in $\text{CaF}_2:\text{Tm}^{2+}$ is therefore quite possible.

§4. THE HEATING OF THE SSR OF THE Cr^{3+} IONS IN RUBY UNDER TRANSVERSE MODULATION OF THE STATIC MAGNETIC FIELD

As in the case of CaF_2:Tm^{2+}, the change ΔS_e in the shape of the OD EPR line of the transition $+1/2 \rightarrow -1/2$ in the Cr^{3+} ion in Al_2O_3 is rather naturally ascribed to the heating of the electron SSR upon absorption of energy from the modulation field. It is easy to show that the cross-relaxation effects in ruby[4,10,12] for $\theta < 1°$ in the given field H_0 should be insignificant. The observed frequency dependence of $S_e^M(\nu_2)$ in ruby, which is linear in the interval 10–20 MHz (see Fig. 5), is consistent[7] with the assumption that the absorption mechanism operating in ruby is absorption in forbidden transitions at low frequencies. The expected value of ΔS_e^M in ruby for this mechanism under conditions of high saturation of the EPR line[1] can be estimated by assuming $\tau_{SSL} = \tau_1/3$ for the SSR of the Cr^{3+} ions. From expressions (2) (for $s \rightarrow \infty$, see Ref. 2) and (9), with $T_2 = 10^{-8}$ sec, $\tau_1 = 0.4$ sec (see Ref. 1), $\nu_2 = 20$ MHz, and $H_2 = 1$ G we obtain

$$\Delta S_e^M(s \rightarrow \infty) \approx \Delta w/4w = {}^1/_{12}\tau_1 \Delta w = 0.15, \tag{13}$$

a value somewhat higher than in experiment (see Fig. 5).

It is noteworthy that in ruby the function $\Delta S_e^M(\nu_2)$ has three peaks in the interval $\nu_2 = 25$–30 MHz (Fig. 5), at frequencies which were observed in a study[13] of the ENDOR in Al_2O_3:$^{53}Cr^{3+}$ and correspond to transitions between the nuclear sublevels of the odd isotope ^{53}Cr at crystal orientations $\theta < 1°$. The observed peaks are thus the spectrum of the OD ENDOR of the ^{53}Cr nuclei (at an extremely low concentration $\simeq 2 \times 10^{-3}\%$); the high intensity of these peaks is explained by the existence of a strong coupling of the electron SSR and the ^{53}Cr nuclei.[14]

§5. CONCLUSION

It has been shown in this study that the electron SSR in CaF_2:Tm^{2+} and Al_2O_3:Cr^{3+} absorbs energy from a low-frequency alternating field orthogonal to the static magnetic field. In view of the fact that the absorption of the SSR is detected by the change in the OD EPR signal, this method might be called the "optically-detected double-Zeeman spin-spin resonance method." The mechanism of absorption of the transverse low-frequency field in ruby is evidently absorption by the spin system in forbidden transitions at low frequencies. It is possible that in CaF_2:Tm^{2+} there is a large contribution from a cross-relaxation mechanism due to the presence of an extraneous paramagnetic impurity. Regardless of the mechanism of the heating of the SSR under transverse modulation, a study of the corresponding effects in the OD EPR spectra yields the cooling coefficient E_{SS} of the SSR and its dependence on the detuning and intensity of the microwave pump.

Our treatment of the influence of a transverse low-frequency field on the electronic spin system is a simplified one, since it takes into account the heating of the electron SSR only. In the case of an inhomogeneously broadened EPR line it is obviously necessary to incorporate the heating of the electronic difference subystem,[8] and also the heating of the nucler Zeeman subsystem through excitation of forbidden electron–nuclear transitions involving the simultaneous reorientation of several electronic and nuclear spins (these questions have not been studied theoretically). In the experiments which have been done it is evidently difficult to distinguish the heating of the SSR, difference, and nuclear subsystems, since these subsystems are usually found in intimate thermal contact.[8]

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1) The mechanism proposed in Ref. 5 for the absorption of the transverse modulation field "at the wings of the spin packets" does not explain certain experimental results and is not considered here.

2) Formulas (6) and (7) are derived in Ref. 7 for spin ensembles with magnetic-resonance lines homogeneously broadened by dipole–dipole interactions. Evidently, these formulas can also be applied to the case of inhomogeneously broadened lines.[9] In any case, the estimates of $P^{(0)}$ made in the present study for an inhomogeneous EPR line from the measured power $P^{(2\omega_0)}$ are justified, since the absorption at low frequencies is of the same nature as that in the region of the $2\omega_0$ satellite.[6,7]

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