Effect of a low-frequency magnetic field on NMR and dynamic nuclear polarization of nuclei in $Al_2O_3:Cr^{3+}$ and $CaF_2:Tm$

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It has been found that low-frequency modulation (longitudinal or transverse) of an external magnetic field leads to a decrease in the NMR absorption signals, and in the presence of microwave pumping it leads to a weakening of the dynamic polarization of the nuclei of the lattice in $Al_2O_3:Cr^{3+}$ and $CaF_2:Tm$ crystals. The dependences of the effect on modulation frequency (up to 30 MHz) and on microwave pumping were studied at liquid helium temperatures. The effect of modulation in ruby is attributed to heating of the spin-spin reservoir (SSR) of the Cr^{3+} ions in direct thermal contact with the ^{27}Al nuclei. The effect of transverse modulation is due to "forbidden" two-spin transitions of the Cr^{3+} ions and that of longitudinal modulation to modulation saturation of the SSR. No direct thermal contact was observed between the electron SSR and the ^{19}F nuclei in $CaF_2:Tm$ and the nature of the observed modulation effects remains an open question.

§1. INTRODUCTION

It was found earlier[1,2] by optical methods for detecting electron paramagnetic resonance (OD EPR) that the energy of a low-frequency (LF) magnetic field orthogonal to the constant magnetic field $\mathbf{H}_0$ was absorbed by the electron spin–spin reservoir (SSR) of transition ions in $Al_2O_3:Cr^{3+}$ and in $CaF_2:Tm$. The phenomenon observed there was used to determine the inverse SSR temperature, β_{SS}, under conditions of microwave pumping. In the present work, to verify the method developed for determining spin temperature and to elucidate the interaction mechanism of the electron SSR and the Zeeman subsystem of the lattice nuclei, the effect of an LF field, both parallel and orthogonal to $\mathbf{H}_0$ (i.e., the effect of longitudinal and transverse modulation of $\mathbf{H}_0$) on NMR in the absence of microwave pumping and on dynamic nuclear polarization (DNP) was studied in the same materials.

§2. MATERIALS STUDIED AND EXPERIMENTAL RESULTS

Crystals of $Al_2O_3:Cr^{3+}$ and $CaF_2:Tm$ identical to those described before,[1,4] were used. The chromium ion concentration in ruby was 0.02 mole %. After growth, the calcium fluoride crystals contained trivalent thulium. The concentration of Tm^{3+} ions was that determined in the batch and was 5×10^{19} cm^{-3} (specimen 1) and 1×10^{19} cm^{-3} (specimen 2). In addition, specimens 2, grown from natural fluorite, contained other rare-earth impurities with total concentration not more than 10^{18} cm^{-3}. Partial reduction of the ions, $Tm^{3+}\rightarrow Tm^{2+}$, was carried out by radiation (specimen 1) and additive coloration (specimen 2). We note that the di- and trivalent states of thulium ions in CaF_2, also produced by thermal treatment (see below), were also identified by the optical absorption spectra.[6] The Tm^{2+}-ion concentration, which amounted after coloring to $n_0\approx1\times10^{18}$ cm^{-3} (specimen 1) and 2.4×10^{18} cm^{-3} (specimen 2), was also determined from these measurements with an uncertainty of about $\pm20\%$.[5] Even after coloring, the $CaF_2:Tm$ specimens thus contained a dominant concentration of Tm^{3+} ions as well as Tm^{2+} ions. We recall that the effective spin of Tm^{2+} ions $S'=\frac{1}{2}$, while the Tm^{3+} ion contains in even number of unpaired electrons.

It was found in studying NMR of ^{27}Al in $Al_2O_3:Cr^{3+}$ in the absence of microwave pumping that a transverse LF modulation of the magnetic field with frequency ν_2 from 0.1 to 3 MHz leads to a weakening of the NMR signal. This effect is independent of the angle θ between the crystal axis and $\mathbf{H}_0$ and of the magnitude of H_0 in the range 2.9 to 3.4 kG, within the limits of the accuracy of measurement ($\pm20\%$), if the angle θ is not more than 5°. For example, for a modulation amplitude $H_2=1$ G, and a modulation frequency $\nu_2=16$ MHz, the relative weakening of the NMR signal $\Delta E_I{}^L$ is about 0.16. The dependence of $\Delta E_I{}^L$ on ν_2 was the same as the frequency dependence of the modulation effect in OD EPR (see Fig. 5 of Ref. 2). The effect of transverse modulation on NMR becomes unobservable when the field H_0 is increased to 7.1 kG, i.e., the magnitude of $\Delta E_I{}^L$ decreases not less than fivefold. On the other hand, the effect rises sharply in the range of angles θ from 10 to 15° and depends strongly on the magnitude of H_0. At $\theta=12.8°$, $H_0=3.0$ kG and $H_2=1$ G, for example, practically total disappearance of the NMR signal is observed, and it is decreased 50% when H_0 deviates by ±40 G from the value given.[1)] Measurements were also made in ruby for orientation $\theta<5°$ with longitudinal modulation of H_0. In this case the $\Delta E_I{}^L$ effect was considerably less (by no less than 5 times).

The effect of LF modulation was also observed under conditions of microwave pumping at a frequency $\nu_1=8.9$ GHz operating in the region of the $+\frac{1}{2}\rightarrow-\frac{1}{2}$ transition in the EPR spectrum of Cr^{3+} ions and producing dynamic polarization of ^{27}Al nuclei.[8] In this case the amplification coefficient of nuclear polarization E_I was measured in the absence and presence of LF modulation and its absolute and relative changes, $\Delta E_I=\Delta\beta_I/\beta_L$ and $\Delta E_I/E_I=\Delta\beta_I/\beta_I$, were determined, where β_I and β_L are the inverse tempera-

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tures of the nuclear Zeeman subsystem and of the lattice, while the symbol Δ indicates the increases in value which occurs on switching on the LF field. It turned out that for transverse modulation $\theta \approx 0°$ the ratio $\Delta E_I/E_I$ is weakly dependent on the detuning Δ_e of the microwave frequency from the center of the EPR line. For detuning corresponding to the maximum DNP ($|E_I| \approx 20$), the value of $\Delta E_I/E_I$ is about half the value of $\Delta E_I{}^L$ observed without microwave pumping. Switching on parallel modulation with amplitude $H_2 = 1$ G under conditions of DNP at not too large detunings (less than the EPR linewidth) led to the disappearance of nuclear polarization: $\beta_I \to 0$.

The effect of LF modulation with frequency ν_2 from 0.1 to 30 MHz on the ^{19}F NMR signal at $T = 1.8$ K in the field range $H_0 = 1.4$ to 5 kG was studied in CaF_2:Tm. In this material a decrease in NMR signals was observed for both transverse and longitudinal modulation. In the first case, the magnitude of $\Delta E_I{}^L$ was about double that in the second and depended very weakly on H_0: on increasing H_0 over the interval stated $\Delta E_I{}^L$ decreased by only 30%. The dependence of $\Delta E_I{}^L$ on the LF field frequency is shown in Fig. 1. This dependence is practically the same for longitudinal and transverse modulation. We note that for transverse modulation with the parameters $\nu_2 = 25$ MHz and $H_2 = 1$ G, the values of $\Delta E_I{}^L$ are about 0.2 and 0.4 respectively for specimens 1 and 2.

Switching on microwave pumping power in the strong field region of the EPR line of the Tm^{2+} ions in CaF_2 led, as for ruby, to the DNP efect. The dependence of the coefficient of cooling of the nuclear subsystem E_I under these conditions on the detuning $\Delta_e = \gamma_1(H_0 - H_0^{\max})$ is shown in Figs. 2 and 3, where γ_1 is the gyromagnetic ratio for Tm^{2+} ions and $H_0^{\max} = 1950$ G is the position of the center of the EPR line. For comparison, values of the cooling coefficient of the electronic SSR, $E_{SS} = \beta_{SS}/\beta_L$, measured under identical conditions,[2] are shown in the same figures. The dependence of E_{SS} on detuning is not shown near the center of the EPR line since the uncertainty in the experimental determination of E_{SS} by the OD method is large for small detunings.

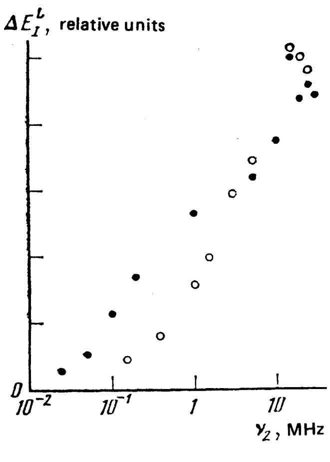

FIG. 1. Weakening $\Delta E_I{}^L$ of ^{19}F NMR signals, on switching-on transverse modulation of the magnetic field, as a function of modulation frequency ν_2, for CaF_2:Tm specimens 1 (○) and 2 (●). The abscissa scale is logarithmic, the ordinate scale is linear.

A decrease in the polarization of the ^{19}F nuclei was observed following application of either transver or longitudinal modulation under DNP conditions. The corresponding changes of ΔE_I are shown as functions of the detuning in Figs. 4 and 5. We determined also the time of τ_n of nuclear-polarization damping after the microwave pumping was turned off, namely 0.6 and 5 sec for samples 1 and 2 respectively. We note that when the temperature was raised from 1.8 to 4.2 K the time τ_n and the effect $\Delta E_I{}^L$ decreased by an approximate factor of 5.

In order to elucidate the role of Tm^{2+} ions in nuclear spin-lattice relaxation processes and in the mechanism of modulation weakening of the NMR signals of ^{19}F nuclei, one of the specimens (number 1) was annealed at $T = 1000$ K. Almost complete charge transfer $Tm^{2+} \to Tm^{3+}$ then took place. It turned out, however, that the removal of Tm^{2+} ions from the specimen did not lead to any change in $\Delta E_I{}^L$ and in its frequency dependence $\Delta E_I{}^L(\nu_2)$. The nuclear spin-lattice relaxation time in the annealed specimen was as before equal to τ_n.

§3. DISCUSSION OF RESULTS FOR $Al_2O_3:Cr^{3+}$

It was shown[2] that transverse modulation of the constant magnetic field leads to heating of the electron SSR, and it appears that in ruby at the $\theta \sim 0°$ orientation the mechanism of LF field absorption via "forbidden" two-spin transitions act. It is known[8,9] that in ruby the SSR of the Cr^{3+} ions is in direct thermal contact with the nuclear subsystem, so that transverse modulation should also lead to heating of the nuclear subsystem and to weakening of the NMR signals in the absence of microwave pumping, as is observed experimentally. The absence (or very small value) of the $\Delta E_I{}^L$ effect at orientations $\theta < 5°$ for longitudinal modulation is explained in this case by the fact that the probability of "forbidden" LF transitions is, according to theory,[10] about $(\omega_{SS}^2/\omega_0^2)^{-1} \sim 10^4$ times less than for transverse modulation (ω_{SS} is the mean SSR frequency and $\omega_0 = \gamma_1 H_0^{\max}$). The appreciable weakening of the $\Delta E_I{}^L$ effect on increasing the field H_0 to 7.1 kG is evidently due to the $\sim \tau_1 H_0^{-2}$ dependence typical of SSR heating mechanism considered,[2] and it is necessary to take account here of the reduction in the electron spin-lattice relaxation time τ_1 with increasing H_0.

We shall now compare the value of $\Delta E_I{}^L$ measured here with the relative change in OD EPR signal which arises under the action of an analogous transverse LF field. Comparison of the results given in §2 with earlier results[2] shows that the relation

$$\Delta E_I{}^L = 4\Delta S_e^{\max} \tag{1}$$

is observed, where $S_e^{\max}$ is the maximum value of the modulation effect in OD EPR, attained at optimal detuning $\Delta_e/\gamma_1 = \pm 65$ G.[4] Both quantities in Eq. (1) depend on the extent of the modulation heating of the electron SSR, $\Delta E_{SS}^L = \Delta\beta_{SS}/\beta_L$. In fact, the kinetic equation for inverse temperature β_I under the conditions considered has the form[8]

$$\frac{d\beta_I}{dt} = -\frac{\beta_I-\beta_L}{\tau_{IL}} - \frac{\beta_I-\beta_{SS}}{\tau_{ISS}}, \tag{2}$$

where τ_{IL} is the nuclear spin-lattice relaxation time through any channel except interaction with the SSR, and τ_{ISS} is the relaxation time of the nuclear Zeeman subsystem to the SSR. It follows from Eq. (2) that modulation heating of the SSR leads to a corresponding heating of the nuclear subsystem:

$$\Delta E_I^L = \Delta E_{SS}^L [1 + (\tau_{ISS}/\tau_{IL})]^{-1}. \tag{3}$$

On the other hand, as follows from Ref. 2,

$$\Delta E_{SS}^L = \frac{\Delta w}{w - \Delta w} \approx \frac{\Delta w}{w} = \frac{\omega_0^2 \Delta S_e^{max}}{a \omega_{SS}^2 (E_{SS}^{max})^2}, \tag{4}$$

where $\Delta w^{-1} = \tau_{SSL}$ is the spin-lattice relaxation time of the SSR: Δw is the rate of heating of the SSR by a transverse LF field, $a = \tau_1/\tau_{SSR}$, and $E_{SS}^{\max}$ is the coefficient of cooling of the SSR at the optimal detuning of the microwave pumping. For sufficiently strong EPR saturation we have[8]

$$E_{SS}^{max} = \pm \omega_0 / 2\omega_{SS}\sqrt{a}.$$

Substituting this value into Eq. (4) we obtain

$$\Delta E_{SS}^L = 4 \Delta S_e^{max}. \tag{5}$$

On comparing Eq. (5) with the experimental relation (1), it follows directly that $\Delta E_I^L = \Delta E_{SS}^L$, i.e., $\tau_{ISS} \ll \tau_{IL}$. This indicates the existence of strong interaction ("direct thermal contact") between the electron SSR of the Cr^{3+} ions and the ^{27}Al nuclear Zeeman subsystem. Such a contact was found earlier in ruby by other methods.[9,11]

The experimental results and the theoretical estimates show that the effect of cross relaxation between different levels of Cr^{3+} ions can be neglected in the range $H_0 = 2.9$ to 3.4 kG for $\theta < 5°$. However, the strong weakening of NMR signals upon transverse modulation of the constant magnetic field in the range $\theta = 10$ to 15° is due to the existence of a cross relaxation point $\nu_{23} = \nu_{34}$,[9] and the width of the cross relaxation maximum corresponds to a detuning $\nu_{23} - \nu_{34} = \pm 200$ MHz, which is in good agreement with the results of other work.[9,11] Finally, it is natural to associate the strong weakening of the DNP effect at $\theta < 5°$ under the action of a longitudinal LF field (see §2) with the heating of the electron SSR because of "modulation saturation."[9,12]

The effect of modulation of the magnetic field on NMR and DNP in Al_2O_3:Cr^{3+} at $\theta < 5°$, described in §2, thus agrees completely with the model of heating of the electron SSR (recognizing that $E_I = E_{SS}$) due to "forbidden" transitions for transverse modulation and due to "modulation saturation" for longitudinal modulation. As we shall see shortly, this "correct" behavior of the electron-nuclear spin system in Al_2O_3 is in sharp contrast with results obtained in CaF_2:Tm.

§4. DISCUSSION OF RESULTS FOR CaF_2:Tm

As in the case of Al_2O_3:Cr^{3+}, it would be natural to associate the weakening of NMR signals under LF modulation of the constant magnetic field in CaF_2:Tm with the heating up of the electron SSR and of the nuclear subsystem in thermal contact with it. However, the situation in CaF_2:Tm is considerably more complicated.

First of all, a study of CaF_2:Tm specimens both containing and not containing Tm^{2+} ions show that the "ΔE_I^L effect" (modulation weakening of the NMR signal in the absence of microwave pumping) is not connected with the Tm^{2+} ions and is explained by the presence in the specimens (including specimen 2) of a "foreign" paramagnetic impurity, apparently Tm^{3+} ions,[2] in an appreciable concentration. Further, the existence of the ΔE_I^L effect both for transverse and longitudinal modulations, and also the sublinear frequency dependence of $\Delta E_I^L(\nu_2)$ (see Fig. 1) do not conform to the model of "forbidden" two-spin LF transitions, but are rather typical of a cross-relaxation mechanism for heating the SSR upon modulation.[2,9;2)] Finally, it is to be noted that the $\Delta E_I^L(\nu_2)$ dependence is noticeably shifted into the region of high frequencies ν_2 compared with the frequency dependence of the $\Delta S_e^{\max}(\nu_2)$ effect typical of heating of the SSR (compare Fig. 1 of the present work with Fig. 2 of Ref. 2).

We shall now go on to discuss the results obtained under conditions of microwave pumping of the EPR line of Tm^{2+} ions. We start with the question of the DNP mechanism. As can be seen from Fig. 2, for detunings Δ_e not ex-

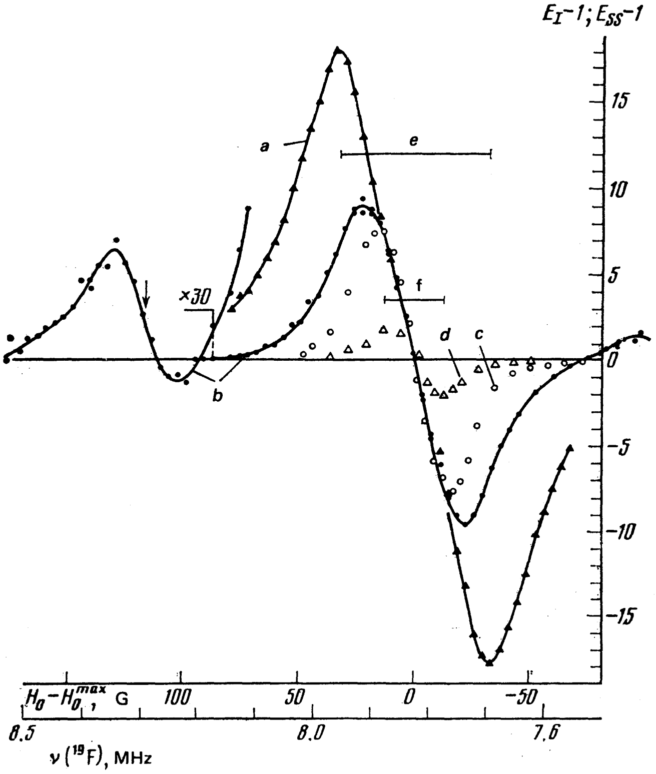

FIG. 2. CaF_2:Tm specimen 2. Experimental dependences of $E_{SS} - 1$ (*a*) and $E_I - 1$(*b–d*) on detuning of the microwave pumping from the center $H_0^{\max}$ of the EPR line of the Tm^{2+} ion. Microwave pumping intensity $H_1^2 = 0.6\ G^2$ weakened by 0 dB (*a,b*), 30 dB (*c*), 50 dB (*d*). Section *e* corresponds to the width of the OD EPR line[2] for $H_1^2 = 0.6\ G^2$; *f* corresponds to the EPR line (as $H_1^2 \to 0$). The change in ^{19}F NMR frequency as a function of detuning is also marked on the *x* axis.

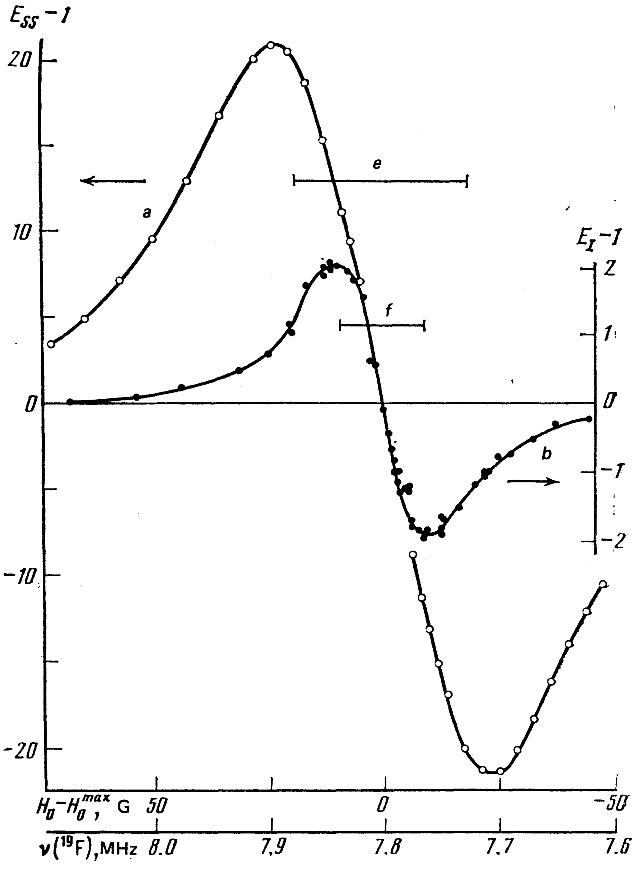

FIG. 3. The same as in Fig. 2, but for specimen 1. The scale of curve *b* is enlarged fourfold relative to curve *a*, see text.

ceeding the half-width of the EPR line, the values of β_I and β_{SS} in specimen 2 practically coincide, which is evidence of good thermal contact between the electron SSR and the ^{19}F nuclei. At the same time, this contact is drastically weakened for large detunings: the nuclear polarization is appreciably weaker than E_{SS}. This indicates that in the present system the thermal contact is not "direct" as in ruby, but "induced," i.e., comes about by the action of microwave pumping, which leads to a simultaneous saturation of both "allowed" and "forbidden" (electron-nuclear) transitions.[8] We introduce the factor

$$\sigma=\frac{\beta_I-\beta_L}{\beta_{SS}-\beta_L}=\frac{E_I-1}{E_{SS}-1}, \tag{6}$$

which characterizes the strength of the thermal contact between the SSR and the nuclei. Evidently $0\leqslant\sigma\leqslant 1$, where the left-hand equality corresponds to the absence and the right-hand to the maximum contact effectiveness. For small detunings $|\Delta_e|$ in specimen 2 we thus have $\sigma=\text{const}\approx 1$, and for large detunings $\sigma\to 0$. From Fig. 3 we see that for specimen 1 there is a similar situation, except that even near the center of the EPR line the thermal contact remains insuffiently effective: $\sigma=\text{const}\approx 1/4$ (for convenience, the values of E_I-1 are shown on that figure in a scale increased fourfold).

We note that the weakness of the contact between the SSR of Tm ions and ^{19}F nuclei under the action of microwave pumping in the wings of the EPR line is explained by our unsuccessful attempts to observe the OD ENDOR effect on distant ^{19}F nuclei by the method described earlier.[4]

The existence of DNP of ^{19}F under microwave pumping of the forbidden electronic transition in a system of three interacting Tm^{2+} ions (indicated by the arrow in Fig. 2) should be noticed.

It is easy to show on the basis of the "thermal mixing" model[8] that for the case of induced thermal contact, at small detunings and strong EPR saturation, the following equation should hold

$$E_I-1=-\sigma\frac{\omega_0\Delta_e}{\Delta_e^2+a\omega_{SS}^2+M_2^G+\sigma f\omega_I^2}, \tag{7}$$

and at strong thermal contact ($\sigma=1$) Eq. (1) takes the usual form.[8] Here M_2^G is the second moment of the envelope of the inhomogeneous EPR line, ω_I is the NMR frequency, and f is the loss factor, defined as

$$f=\frac{n_I}{n_a}\frac{\tau_1}{\tau_n},$$

where n_I and n_a are the concentrations of ^{19}F nuclei and of the "active" (saturated by the microwave field) Tm^{2+} ions. Recognizing that $n_a=n_0/2$, while $\tau_1=2\times10^{-3}$ s and 1×10^{-1} s for specimens 1 and 2, we obtain $\sigma/\omega_I^2=2\times10^{17}$ s^{-2} and 2×10^{18} s^{-2} for these specimens. On the other hand, the value of the expression in the denominator of Eq. (7) can be found from the slope of the experimental $E_{SS}(\Delta_e)$ dependence near the center of the EPR line, see Figs. 2 and 3. This gives

$$a\omega_{SS}^2+M_2^G+\sigma f\omega_I^2=(1.1\pm0.2)\cdot10^{18}\ \text{sec}^{-2}$$

and $(2.2\pm0.4)\times10^{18}$ s^{-2} for specimens 1 and 2. From this and using the loss parameters given above, we find for specimen 1 that $a\omega_{SS}^2+M_2^G=(9\pm2)\times10^{17}$ s^{-2}, which is in good agreement with the calculated $(7\pm1)\times10^{17}$ s^{-2} obtained earlier independently.[2] This confirms, in particular, the correctness of the determination of the concentration of active paramagnetic centers (Tm^{2+}) and provides a method for measuring it if not already known.

The contribution of $\sigma f\omega_I^2$ in the denominator of Eq. (7) is the determining term for specimen 2, which indicates that nuclear relaxation through a foreign paramagnetic impurity (apparently Tm^{3+}) is even more important than in specimen 1. Therefore, only the upper limit of $a\omega_{SS}^2+M_2^G\leqslant 6\times10^{17}$ s^{-2} can be estimated. Its value 1.3×10^{18} s^{-2} obtained earlier[2] without taking account of loss, is thus overestimated.

We now turn to the modulation effect (Figs. 4 and 5). As has already been noted, longitudinal modulation of the constant magnetic field under conditions of microwave pumping of the EPR line leads to heating of the electron SSR: $\beta_{SS}\to 0$ (the modulation-saturation mechanism is described elsewhere[9,12]), and the energy of the modulating field absorbed by the SSR is proportional to the form factor of the EPR line.3) This explains the dependence of the effect of longitudinal modulation on the detuning in Figs. 4,b and 5,b. We note that this effect changes sign on passing from one wing of the EPR line to the other, as does the magnitude of β_{SS}. For a small detuning $\Delta_0\ll T_2^{-1}$, where T_2^{-1} is the half-

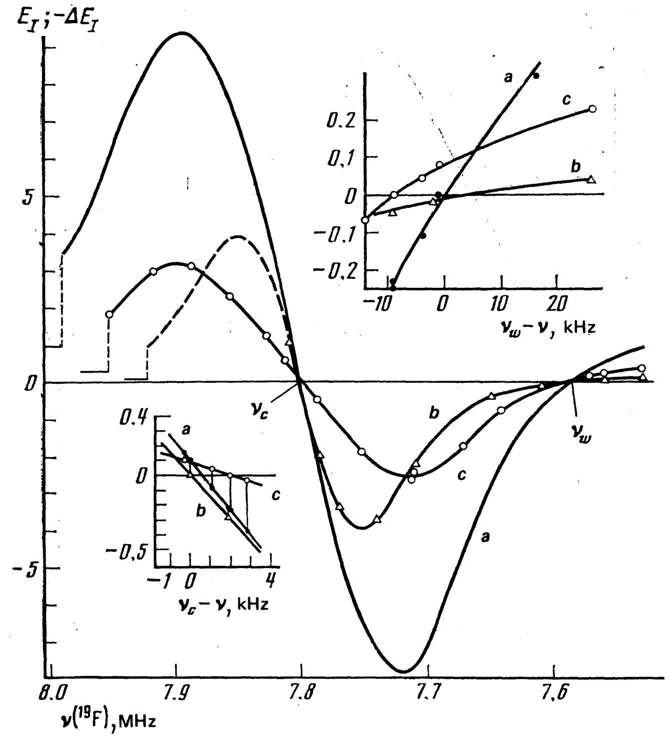

FIG. 4. CaF$_2$:Tm specimen 2. Experimental dependences of $E_I(a)$ and $\Delta E_I(b,c)$ for longitudinal (b) and transverse (c) modulation (with frequency $\nu_2 = 0.38$ MHz) of the constant magnetic field on the magnitude of this field (in units of the ^{19}F NMR frequency) near the EPR line of the Tm^{2+} ion. The intensity of microwave pumping is $H_1^2 = 0.6$ G^2. The amplitude of the modulating field H_2 are 1.4 G (b) and 2.4 G (c). The insets show in an enlarged scale curves a–c in the neighborhood of $E_I = 0$ for microwave pumping near the center (point ν_c) and on a wing (point ν_w) of the EPR line. The horizontal sections on curves a–c show the signal level in the absence of microwave pumping.

width of the EPR line a value of $E_I(\Delta_0)$ can be found which does not change when parallel pumping is turned on (point ν_c in Figs. 4 and 5). Obviously $\beta_{SS} = 0$ for this detuning. This enables the parameter σ, introduced above, to be determined with great accuracy by measuring the amplitude of the NMR signal under the action of microwave pumping at the value ν_c. Such measurements gave the values $\beta_I/\beta_L = 0.75 \pm 0.1$ and 0.1 ± 0.02, i.e., when Eq. (6) is taken into account, $\sigma = 0.25 \pm 0.1$ and 0.9 ± 0.02 for specimens 1 and 2, which agrees splendidly with estimates given above and confirms the validity of the model used.

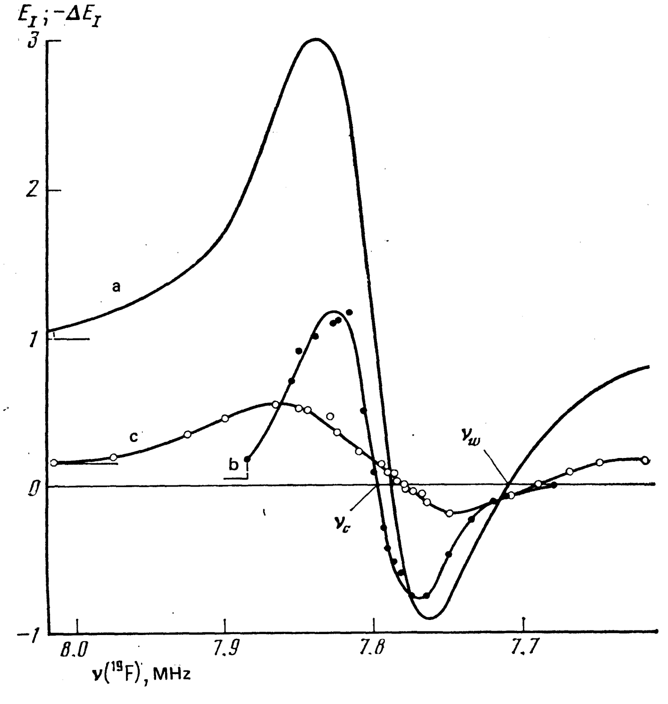

FIG. 5. The same as in Fig. 4, but for specimen 1.

It is considerably more difficult to interpret the results of the action of transverse modulation. As can be seen from Figs. 4 and 5, such modulation under microwave pumping of the EPR line leads at small detunings to unexpected effects: to a reduction in β_I under conditions when $\beta_{SS} = 0$ (point ν_c), and to an inversion of the nuclear subsystem ($\beta_I < 0$) for detuning, where in the absence of modulation $\beta_I = 0$ and $\beta_{SS} < 0$. These facts evidently show that the action of a transverse LF field manifests itself not only in a heating of the electron SSR ($\beta_{SS} \to 0$) but also in a forced mutual approach of the inverse temperature β_{SS} and β_I, i.e., in the appearance of a new additional thermal mixing channel between the SSR of the paramagnetic impurity and the nuclei of the lattice. This conclusion is, however, not applicable to the region of large detunings. We shall consider, for example, the point ν_w on the low-field wing of the EPR line (Figs. 4 and 5). Before switching on the modulation, the value of β_I at the point ν_w passes through zero, while $\beta_{SS} < 0$. A transverse LF field produces in specimen 2 (Fig. 4) at this point a ΔE_I effect of about the same magnitude and sign as at the point ν_c, although the extent of the SSR cooling near point ν_w is incomparably greater (see Fig. 2). The situation is still more complicated in specimen 1 (Fig. 5): at the points ν_c and ν_w the effect of transverse modulation has different signs, although the SSR temperature in both cases is negative.

We cannot at present provide a final experiment of these facts and also of the features of modulation heating of the ^{19}F nuclear subsystem in the absence of microwave pumping, as noted above. We can suppose that "forbidden" electron–nuclear transitions induced by the LF field in which no less than three spins, for example two electronic and one nuclear, are involved, play an important part here. Estimates show that the probabilities of such processes, determined by nonsecular terms of the electron-nuclear dipole interaction, are in principle high enough to explain the observed effects. However, there is as yet no corresponding rigorous theory.

5. CONCLUSIONS

In the present work the effect of low-frequency transverse modulation of the constant magnetic field on NMR and DNP in dielectric crystals containing paramagnetic impurity has been found for the first time. The effect in Al_2O_3:Cr^{3+} can be attributed to heating of the electron SSR upon saturation of forbidden two-spin LF transitions in the ensemble of Cr^{3+} spins by the modulating field, and as a consequence to heating of the nuclear Zeeman subsystem which is in direct thermal contact with the SSR. In CaF_2:Tm, heating of the nuclear subsystem takes place both for transverse and longitudinal modulation of the magnetic field, and the absence of direct thermal contact between the SSR and the nuclei evidently points to excitation of "forbidden" electron-nuclear transitions under the action of the LF modulation field. These results require further development of the theory of spin dynamics in systems of interacting electronic and nuclear spins.

[1] A similiar effect was observed before.[7]

[2] According to theory,[13] longitudinal modulation of the magnetic field also leads to an "instrumental" decrease of the peak intensity of the NMR line by about $J_0^2(\gamma_2 H_2/2\pi\nu_2)$ times, where J_0 is a Bessel function and γ_2 is the nuclear gyromagnetic ratio. However, this parasitic effect is insignificant in our case compared with the observed magnitude of $\Delta E_r{}^L$.

[3] We are not discussing here the effect of inhomogeneous EPR line broadening on the modulation-saturation effect.

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