[1] R. Jengo and E. Remiddi, Preprint TH 1050-CERN, 1969.
[2] H. Suura, Phys. Rev. Lett. 23, 551 (1969).
[3] Y. Oyanagi, Progr. Theor. Phys. 42, 898 (1969); Nucl. Phys. B14, 375 (1969); M. Tokuda and Y. Oyanagi, Phys. Rev. D1, 2626 (1970).
[4] P. Frampton, Phys. Rev. D1, 3141 (1970).
[5] G. Veneziano, Nuovo Cim. 57A, 190 (1968).
[6] C. Lovelace, Phys. Lett. 28B, 264 (1968).
[7] Di Giacomo et al., Phys. Lett. 33B, 171 (1970).
[8] E.T. Whittaker and G.N. Watson, Modern Analysis, Cambridge, 1927.
[9] C.W. Akerlof et al., Phys. Rev. 163, 1482 (1967); C. Mistretta et al., Phys. Rev. Lett. 20, 1523 (1968); J.E. Augustin et al., Lett. Nuovo Cim. 2, 214 (1969).
[10] T.C. Chia et al., Phys. Rev. D1, 2126 (1970).

"FORBIDDEN" CROSS-RELAXATION TRANSITIONS AND THEIR ROLE IN THE DYNAMICS OF STATIONARY ENDOR

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The frequencies of the electron-nuclear double resonance (ENDOR) are due to the hyperfine interaction (HFI) of the electron of the paramagnetic center with the lattice nuclei. If the electron spin of the center is $S = 1/2$, then each nucleus gives two ENDOR frequencies for radio frequency (RF) transitions with $M = 1/2$ and $M = -1/2$, respectively (M is the projection of $\vec{S}$ on the external magnetic field $\vec{H}$). In the simplest case these frequencies [1, 2] are

$$\nu_{\mp 1/2} = \left|\frac{1}{2}a + \frac{1}{2}b(3\cos^2\theta - 1) \pm \nu_n\right|. \quad (1)$$

where a and b are the constants of the isotropic and anisotropic HFI with the nucleus, ν_n is the Larmor frequency of the nucleus, and θ is the angle between the axial axis of the HFI and $\vec{H}$. The frequencies $\nu_{-1/2}$ and $\nu_{1/2}$ are customarily called the summary and differential frequencies. We confine ourselves to a very simple model, which retains the main features of the real multilevel system, namely, we consider a paramagnetic center with $S = 1/2$ and two nuclei with spins $I_1 = I_2 = 1$. Let $a_1 \gg a_2$ and $|b_i| \ll a_i$ ($i = 1, 2$). Figure 1 shows the energy levels of our system; the frequencies (1) are determined by the selection rules $\Delta M = 0$, $\Delta m_1 = \pm 1$, $\Delta m_2 = 0$, $\Delta m_1 = 0$, $\Delta m_2 = \pm 1$, where m_1 is the projection of $\vec{I}_1$ on $\vec{H}$ and m_2 is the projection of $\vec{I}_2$ on the quantization axis $n(M)$, which does not coincide with $\vec{H}/H$ if

$$\left|\frac{1}{2}a_2 - \nu_{n2}\right| \sim b_2$$

(see [2]), and depends on M.

Great interest attaches to the dynamics of the stationary ENDOR [3, 4] for the study and separation of different relaxation processes in multilevel systems. One of the questions that has remained unanswered for ten years is that of the difference between the intensities δ of the ENDOR signals of paramagnetic centers at the summary and difference frequencies: $\delta_c \neq \delta_p$ (in particular, for F centers in a number of alkali-halide crystals, see [3]). It was shown experimentally in [5] that the effect $\delta_c \neq \delta_p$ is due to the inclination of the quantization axis (IQA) of the nuclei of one of the coordination spheres of the

F centers relative to the direction of $\vec{H}$. In the present paper we propose a mechanism that explains how the IQA of the nuclei of one of the coordination spheres leads to the effect $\delta_c \neq \delta_p$ at the nuclei of all the other coordination spheres, and explain the experiments of [3] on the angular dependence of δ_c/δ_p.

To find δ it is necessary to determine the stationary populations $n_{Mm_1m_2}$ of the levels (Fig. 1) under ENDOR conditions (microwave transitions in the center of the EPR line). We obtain $n_{Mm_1m_2}$ by solving the equations for the populations ($\sum n_{Mm_1m_2} = N$, N is the total number of the centers)

$$0 = \frac{dn_{Mm_1m_2}}{dt} = \left(\frac{dn}{dt}\right)^{rel}_{Mm_1m_2} + \left(\frac{dn}{dt}\right)^{c.rel}_{Mm_1m_2} + \left(\frac{dn}{dt}\right)^{ind}_{Mm_1m_2}. \qquad (2)$$

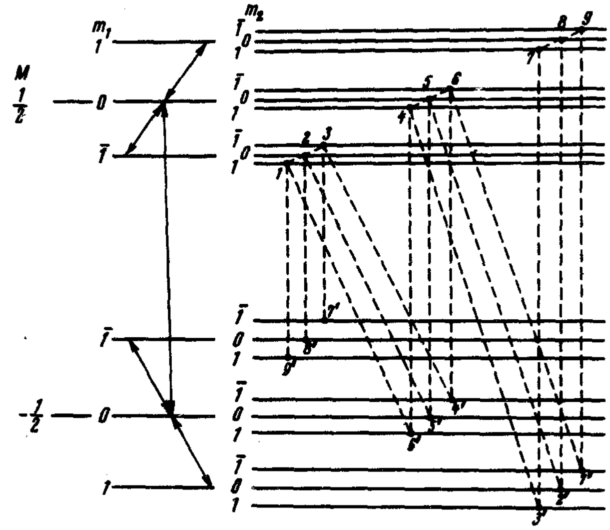

Fig. 1. Energy levels of the model under consideration. The solid lines denote the microwave signal and the RF excitation; the dashed lines denote the relaxation transitions and the transitions generated by the forbidden cross relaxation transitions (1 - 2, 2 - 3, 1 - 3, etc.). RF excitations with M = 1/2 and M = - 1/2 are turned on separately.

The first term takes into account all the possible relaxation transitions (Fig. 1 indicates the most significant of them at $a_1 \gg a_2$: $\Delta M = \pm 1$, $\Delta m_1 = \Delta m_2 = 0$ and $\Delta M + \Delta m_1 = 0$, $\Delta m_2 = 0$). The second term takes into account the microwave and RF transitions (Fig. 1 shows the RF transitions $\Delta M = 0$, $\Delta m_1 = \pm 1$, and $\Delta m_2 = 0$). The third term takes into account the ordinary cross-relaxation transitions (CRT) [6] (if the indices I and II denote different centers, then under the influence of the electronic magnetic dipole-dipole interaction H_{d-d} the possible transitions are $\Delta(M_I + M_{II}) = 0$, $\Delta m_{Ii} = \Delta m_{IIj} = 0$, but $m_{Ii} \neq m_{IIj}$, $i \neq j = 1, 2$).

After finding the populations[1)] and using them to express δ in the usual manner, we obtain $\delta_c \approx \delta_p$ (the difference is due to somewhat different probabilities of the RF transitions to $\nu_{1/2}$ and $\nu_{-1/2}$ [7, 5, 4]). Owing to the IQA of the second nucleus, forbidden induced and relaxation transitions occur (e.g., microwave transitions with $\Delta m_2 \neq 0$, relaxation transitions with $\Delta M = \pm 1$, $\Delta m_2 \neq 0$, $\Delta m_1 = 0$). Their inclusion in (2) does not change the conclusion that $\delta_c \approx \delta_p$ (in contradiction to the assumption made in [5]). An investigation of the matrix of the equations (2) shows that the reason why δ is independent of whether $\nu_{1/2}$ or $\nu_{-1/2}$ transitions are induced is the equality of the probabilities of the relaxation transitions of the types $M, m_1, m_2 \leftrightarrow M', m_1', m_2'$, and $-M, -m_1, -m_2 \leftrightarrow -M', -m_1', -m_2'$.

[1)]The high temperature approximation $g\beta H \ll kT$ is assumed throughout. Equations (2) are quite easy to solve with the aid of the electric simulation model developed by us.

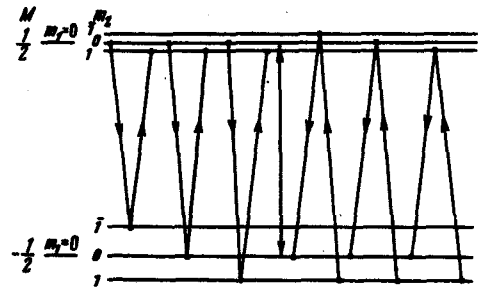

Fig. 2. Inclined lines - some of the FCRT, vertical line - saturating microwave signal.

The situation can change if account is taken of the forbidden CRT (FCRT), which become possible in the case of IQA of the second nucleus and are described by the matrix element

$$\langle M_I m_{I1} m_{I2}, M_{II} m_{II1} m_{II2} | H_{g-g} | M_I' m_{I1} m_{I2}' M_{II}' m_{II1} m_{II2}' \rangle = \langle M_I M_{II} | H_{g-g} | M_I' M_{II}' \rangle \langle m_{I2} | m_{I2}' \rangle \times \langle m_{II2} | m_{II2}' \rangle, \; M_I' + M_{II}' = M_I + M_{II}. \tag{3}$$

Here $|\langle m_2 | m_2' \rangle| = d^I_{m_2 m_2'}(\beta)$, where $d^I_{mm'}(\beta)$ is the Wigner function [8], and $\cos\beta = \vec{n}(M)\cdot\vec{n}(M')$ (see [2]). Figure 2 shows these FCRT, which lead to the appearance of new terms in (2):

$$\left(\frac{dn}{dt}\right)^{FCRT}_{Mm_1m_2} = \sum_{m_2'=-I}^{I} W^{cr}_{Mm_2m_2'} \sum_{m_2''=-I}^{I} \frac{n_{M'm_1m_2''}}{N} [d_{m_2m_2''}(\beta) d_{m_2''m_2'}(\beta)]^2 \times (n_{Mm_1m_2'} - n_{Mm_1m_2}). \tag{4}$$

For magnetically-dilute systems, in accordance with [9], we have

$$W^{cr}_{Mm_2m_2'} = (2T_{cr})^{-1} \exp[-\nu^2_{Mm_2m_2'} (2 \langle \nu^2_{cr} \rangle)^{-1}], \tag{5}$$

where T_{cr} and the second moment $\langle \nu^2_{cr} \rangle$ of the form function of the probability of the CRT depend on the concentration f of the centers [9]. T_{cr} coincides in order of magnitude with the time of the spip-spin relaxation T_2. $h\nu_{Mm_2m_2'}$ is the energy exchanged with the dipole-dipole reservoir in FCRT. If $|m_2 - m_2'| = 1$, then $\nu_{Mm_2m_2'} = \nu_M$ of the second nucleus from (1). For F centers in KBr, the IQA is significant for sphere IV. According to the data of [3] (H = 3380 Oe, $f = 1.07 \times 10^{-5}$) we have for these nuclei $\nu_{1/2} \simeq 0.9$ MHz, $\nu_{-1/2} \simeq 6.6$ MHz, and $[\langle \nu^2_{cr} \rangle]^{1/2} = 1.68$ MHz.

The terms (4) in (2) can be interpreted [6] as being generated by the relaxation transitions $Mm_1m_2 \leftrightarrow Mm_1m_2'$. Since for KBr the exponential in (5) at M = 1/2 is equal to 0.87, and to 0.45×10^{-3} at M = -1/2, the terms (4) are significant only at M = 1/2. These transitions are indicated in Fig. 1.

Let us show that the FCRT leads to $\delta_c > \delta_p$ for ENDOR at the first nucleus. Stationary ENDOR arises as a result of the effective shortening of the relaxation time T_1, by the RF transitions [3, 4]. For relaxation from the state 5 to the state 5' (Fig. 1), RF in the absence of FCRT opens the channels 5 - 2 - 5' at the frequency $\nu_{1/2}$ and 5' - 2' - 5 at $\nu_{-1/2}$. These channels lead to the same effective shortening of T_1 and $\delta_c \simeq \delta_p$. The transitions due to the FCRT lead in addition to the RF also to a connection between the states 5, 2, and 5, 8 (relaxation channels of the type 5 - 4 - 6' - 1 - 2). Therefore turning on of RF excitation between 5, 2, and 5, 8 changes the effective times T_1 less than in the absence of FCRT. To the contrary, at the frequencies $\nu_{-1/2}$ the RF opens, besides the path 5' - 2' - 5, also, as a result of the FCRT, channels of the type 5' - 8' - 2 - 3 - 4' - 6 - 5, and this leads to an additional decrease of T_1. Thus, the FCRT decrease δ_p and increase the δ_c.

The factors d(β) in (4) lead to a dependence of δ_c/δ_p on the angle θ, in quantitative agreement with experiment [3]. This explains also the angular dependence of the effective time T_1 [3] and the dependence of δ_p/δ_c on H [5]. As $f \to 0$ the FCRT effect vanishes, and at sufficiently large f, when $[\langle\nu_{cr}^2\rangle]^{1/2} > \nu_{-1/2m_2m_2}$, the value of $W^{cr}_{Mm_2m_2'}$ does not depend on M, thereby equalizing δ_c and δ_p.

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[1] H. Seidel, Z. fur Physik 165, 218 (1961).
[2] V.Ya. Zevin, S.S. Ishchenko, and M.A. Ruban, Zh. Eksp. Teor. Fiz, 55, 2108 (1968) [Sov. Phys.-JETP 28, 1116 (1969)].
[3] H. Seidel, Z. fur Physik 165, 239 (1961).
[4] V.L. Gokhman, V.Ya. Zevin, and B.D. Shanina, Fiz. Tverd. Tela 10, 337 (1968) [Sov. Phys.-Solid State 10, 269 (1968)].
[5] W.T. Doule and T.E. Dutton, Phys. Rev. 180, 424 (1969).
[6] N. Blombergen, S. Sapiro, P.S. Pershon, and T.O. Artman, Phys. Rev. 114, 445 (1959).
[7] A.B. Roitsin, Ukr. Fiz. Zh. 10, 147 (1965).
[8] V.V. Berestetskii, E.M. Lifshitz, and L.P. Pitaevskii, Relativistskaya kvantovaya teoriya (Relativistic Quantum Theory), Nauka, 1968, Part I, p. 470.
[9] A.Kiel, Phys. Rev. 125, 1451 (1962).

INSTABILITY OF SPIN WAVES IN FERROELECTRIC ANTIFERROMAGNETS IN EXTERNAL FIELDS

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At the present time we know of a considerable number of ferroelectric magnetically-ordered cyrstals - antiferromagnets and weak ferromagnets (see the review [1]). We shall show that in such crystals it is possible to excite parametrically spin waves by an external electric field. The mechanism of this excitation is close to the known mechanism of parametric excitation of spin waves by an external alternating magnetic field [2], although the two are not equivalent.

Excitation of spin waves is easiest to realize in a crystal under conditions close to critical (i.e., at values of the external magnetic field, temperature, and pressure close to the critical values at which a phase transition takes place in the magnetic system of the crystal). This is due to the fact that in the vicinity of the critical point a relatively small alternating electric field suffices for excitation of the spin waves.

We consider the excitation of spin waves by an alternating electric field in a ferroelectric antiferromagnet in the presence of a constant magnetic field H_0. As an example of the critical point, we analyze the case $H_0 \sim H_c$, where H_c is the field when the magnetic moments of the sublattices turn over. We show that for spin-wave excitation the amplitude of the electric field should exceed a critical value $e_c = e_c^0[1 - (H_0/H_c)^2]^{1/2}$, where $e_c^0 \sim 300$ V/cm.