Nuclear relaxation via electron-spin cross relaxation

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The mechanism of nuclear relaxation in the vicinity of a paramagnetic center is studied. The hyperfine interaction (HFI) constants of the nuclei are assumed to be of the order of magnitude of the dipole-dipole interaction energy between the paramagnetic centers. The experiments are performed with LiF crystals with F centers by the electron-nuclear double resonance (ENDOR) technique. It is shown that nuclear relaxation of the indicated type is due to cross-relaxation transitions (CRT) of electron spins in various local fields. For such CRT, spin flip of the surrounding nuclei is not required and energy exchange with the electron-spin subsystem is of the order of the HFI energy. It is found that the longitudinal relaxation time T_{in} of the indicated type of nuclei increases with growth of their HFI energy. Values of T_{in} are obtained for various crystal temperatures and F-center concentrations. A number of effects in the ENDOR dynamics are important for the identification and reduction of spectra are detected and explained. An experimental procedure is suggested for determining the shape function of the cross-relaxation probability.

INTRODUCTION

Much attention is being paid lately to the relaxation of nuclei in crystals containing paramagnetic impurities[1,2], since these processes explain the details of the dynamic behavior of nuclear and electron spin systems and play an important role in the polarization of nuclear spins[3].

Up to now, the nuclear relaxation mechanisms in crystals with paramagnetic impurities have been investigated by the NMR method. As a rule, it was impossible to register nuclei in the nearest environment of the paramagnetic center if their hyperfine interaction (HFI) energy was appreciable. It is possible to study relaxation of this type of nuclei only by the electron nuclear double resonance (ENDOR) method, which was indeed used by us in this study. The number of nuclei of this type is much smaller than the number of nuclei that resonate at the Larmor frequency, but is precisely these nuclei which can play an important role in the processes of relaxation and spin diffusion of the bulk of the lattice nuclei.

As is well known,[1] there are two groups of nuclear relaxation mechanisms connected with paramagnetic impurities. The first includes mechanisms based on modulation of the HFI constants by the thermal lattice vibrations (see, e.g.,[4]). The second group of mechanisms is connected with fluctuations of the magnetic field at the nucleus due to the reorientation of the electron spin[1,2]. Spatial spin diffusion of the nuclear spins is difficult for the nearest-environment nuclei, since they resonate at different frequencies.[1]

We have investigated the relaxation mechanism of nuclei with HFI constants on the order of E_{d-d} in LiF crystals containing F centers. We show that the most effective mechanism is relaxation due to cross relaxation of the electron spins. In contrast to the previously considered mechanisms[1,2], there is no direct reorientation of the nuclear spins in the described mechanism, and the T_{1n} of the nuclei does not decrease with increasing HFI constant, but increases.

In the experiments we dealt with inhomogeneously broadened EPR lines with limited cross relaxation[5], so that the effects connected with the change in the temperature of the dipole-dipole pool of the electron spins were insignificant in our experiments[6].

1. EXPERIMENT

The measurements were performed in the 3-cm wavelength band. The objects of the investigation were LiF crystals with different F-center concentrations, at a ratio $N_{II}/N_I \approx 4$, where N_I and N_{II} are the F-center concentrations in samples I and II, with $N_I \approx 4 \times 10^{17}$ cm^{-3}. We investigated the mechanism of relaxation of the Li^7 nuclei of the coordination spheres III and V, and of the F^{19} nuclei of the spheres IV, VI, and VIII, the HFI constants of which are of the order of E_{d-d} (see[8] concerning the HFI constants in LiF).

Each of these nuclei give two ENDOR lines, the frequencies of which can be represented in the form

$$\nu_M^{(i)} = |\nu_n^{(i)} - M[a_i\hbar^{-1} + b_i\hbar^{-1}(3\cos^2\theta_i - 1)]| \equiv |\nu_n^{(i)} - M\Delta\nu_{SI}^{(i)}|, \qquad (1)$$

where a_i and b_i are respectively the isotropic and anisotropic HFI constants of the i-th nucleus, $\nu_n^{(i)}$ is its Larmor frequency, M is the projection of the electron spin on the magnetic field H, and θ_i is the angle between H and the line from the F center to the nucleus. The frequencies $\nu_{-1/2}^{(i)}$ and $\nu_{+1/2}^{(i)}$ are called the sum and difference frequencies, respectively.

For the nuclei of the indicated spheres, we have observed a number of particular effects in the ENDOR dynamics. The intensities δ of the ENDOR lines were not proportional to the number of resonating nuclei, δ decreasing with the decreasing $\Delta\nu_{SI}^{(i)}$, see Fig. 1a. In addition, the intensity ratio of the different ENDOR lines depends significantly on the intensity of the radio-frequency (rf) field H_2 at which they are registered; see Fig. 1b.

A study of the T_{1n} of the nuclei of the indicated spheres was carried out by stationary saturation of the corresponding nuclear transitions by an rf field at the frequencies (1), and from the dependence of the ENDOR linewidth $\Delta\nu$ on H_2. The crystal was rotated in the (001) plane, and the T_{1n} of the nuclei was investigated at different values of $\Delta\nu_{SI}^{(i)}$. It was experimentally established that T_{1n} depends on $\Delta\nu_{SN}^{(i)}$, with the T_{1n} of the

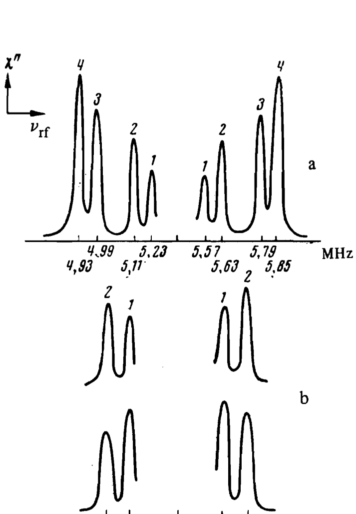

FIG. 1

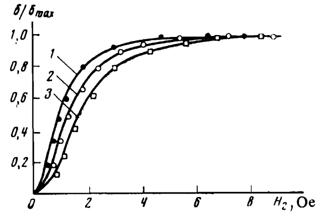

FIG. 2

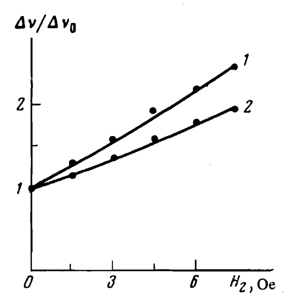

FIG. 3

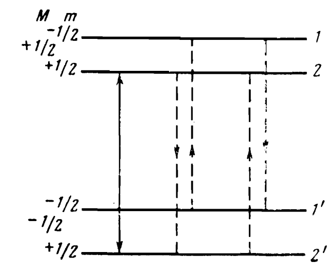

FIG. 4. Energy-level scheme of the considered model. The solid line shows the saturating microwave transition, and the dashed lines show the cross-relaxation transitions.

FIG. 1. a) ENDOR spectrum of sphere V nuclei of Li^7. The values of $\Delta\nu_{SI}^{(i)}$ for lines 1, 2, 3, and 4 are respectively 0.33, 0.48, 0.80, and 0.92 MHz. Lines 3 and 4 are due to pairs of equivalent nuclei, and lines 1 and 2 to groups of four equivalent nuclei; χ'' is the imaginary part of the magnetic susceptibility, and ν_{rf} is the frequency of the rf field in MHz. b) ENDOR spectrum of spheres IV, VI, and VIII of F^{19}. Lines 1 and 2 are due to 10 and eight nuclei, respectively. The upper spectrum was recorded at $H_2 = 0.5$ Oe, and the lower at $H_2 = 3.0$ Oe.

FIG. 2. Plot of δ against H_2 in LiF crystals, T = 300°K. Curves 1 and 2 describe the saturation of the ENDOR lines from groups of four equivalent Li^7 nuclei of spheres III and V in sample I, for which $\Delta\nu_{SI}^{(i)}$ is equal to 1.20 and 0.48 MHz, respectively. Curve 3 characterizes saturation of the same nuclei as curve 1, but in sample II, while δ_{max} is the maximum value of the ENDOR signal.

FIG. 3. Dependence of the width of the ENDOR lines on H_2. Sample I, T = 300°K. Curves 1 and 2 characterize the broadening of the ENDOR lines from a pair of equivalent Li^7 nuclei of sphere V, for which $\Delta\nu_{SI}^{(i)}$ is equal to 0.94 and 0.72 MHz, respectively, and $\Delta\nu_0$ is the width of the ENDOR line in the absence of saturation.

nuclei decreasing with decreasing $\Delta\nu_{SI}^{(i)}$. The effect is determined (like the previously indicated dynamic phenomena) not by the number of the coordination sphere of the nuclei, but by the value of $\Delta\nu_{SI}^{(i)}$. Curves 1 and 2 in Fig. 2 (which are the curves of the saturation of the ENDOR signals by the rf field, normalized to unity) illustrate the described phenomenon. Figure 3 shows the dependence of the ENDOR linewidth $\Delta\nu$ on H_2 for two groups of nuclei with different values of $\Delta\nu_{SI}^{(i)}$. It is seen from Figs. 2 and 3 that the ENDOR signals from nuclei for which $\Delta\nu_{SI}^{(i)}$ is small (at equal H_2) are saturated less strongly than the ENDOR signals from nuclei for which $\Delta\nu_{SI}^{(i)}$ is large. The described effects take place to an equal degree upon saturation of the sum as well as of the difference ENDOR lines.

To determine the dependence of T_{1n} in the concentration of the F centers and on the crystal temperature, we studied the saturation curves of the ENDOR signals from the nuclei of spheres III and V for sample II. It was found experimentally that at equal values of H_2, the ENDOR lines from nuclei with identical $\Delta\nu_{SI}^{(i)}$, are more weakly saturated in sample II (the sample with the larger concentration) than in sample I (see Fig. 2). Measurements performed at T = 300 and 77°K have shown that T_{1n} does not depend on the crystal temperature. The nuclei of coordination spheres I and II have HFI constants that are much larger than E_{d-d}. The dynamic effects described above do not occur in these nuclei, and the time T_{1n} is much shorter than for the nuclei of spheres III-VIII, so that for the nuclei of spheres I-VIII the plot of T_{1n} against $\Delta\nu_{SI}^{(i)}$ is a curve with a maximum.

The described experiments were performed at magnetic-field values H equal to the resonant value H_0. The experiments performed at $H \neq H_0$ did not lead to a noticeable deviation from the experimental plots.

2. DISCUSSION OF RESULTS

To explain the experimental results, let us consider a model system consisting of an electron with spin $S = 1/2$ and a nucleus with spin $I = 1/2$ (see Fig. 4). In the presence of dipole-dipole interaction between the electrons, the saturation of the 2-2′ transition by the microwave field via cross-relaxation transitions (CRT) will be transferred to the transition 1-1′. Additional terms then appear in the equations for the populations (n_i is the population of the i-th level):

$$\left(\frac{dn_2}{dt}\right)_{cr} = W_{21',2'1}^{cr}\frac{1}{N_0}(n_{2'}n_1 - n_2n_{1'}),\quad \left(\frac{dn_{2'}}{dt}\right)_{cr} = -\left(\frac{dn_2}{dt}\right)_{cr}, \tag{2}$$

where N_0 is the total number of centers and $W_{21',2'1}^{cr}$ is the probability of the CRT shown in Fig. 4; we present this probability in the form

$$W_{21',2'1}^{cr} = w_{21',2'1}\,g(\nu_{11'} - \nu_{22'}), \tag{3}$$

where $g(\nu_{11'} - \nu_{22'})$ is the form function of the CRT probability; its width $\Delta\nu_{cr}$, and also $w_{21',2'1}$, depend on the concentration of the paramagnetic centers. At the considered CRT, the energy transferred to the electron-spin system (to its pool of dipole interactions) is $h|\nu_{11'} - \nu_{22'}| = h\Delta\nu_{SI}^{(i)}$, and this energy is transferred in the final analysis to the lattice at the relaxation rate of the dipole pool[2,9].

The factor that arises in (3) because of the form function will be designated $g(\nu_{11} - \nu_{22'}) \equiv g(\Delta\nu_{SI}^{(i)}, \Delta\nu_{cr})$. This factor, as is well known, decreases with increasing $\Delta\nu_{SI}^{(i)}$ at constant $\Delta\nu_{cr}$ (i.e., in one crystal for different nuclei) and increases with increasing $\Delta\nu_{cr}$ at constant $\Delta\nu_{SI}^{(i)}$ (i.e., for the same nuclei in crystals having different paramagnetic-center concentrations).

When the transitions are saturated with microwaves, it can be assumed approximately that $(n_1 - n_2) \approx (n_{2'} - n_{1'})$, and then $(n_{2'}n_1 - n_2n_{1'}) \approx (n_2 + n_{2'})(n_1 - n_2)$. Taking this into account, we rewrite (2) in the form

$$\left(\frac{dn_2}{dt}\right)_{cr} \approx w_{cr}(n_1 - n_2),\qquad \left(\frac{dn_{2'}}{dt}\right)_{cr} \approx w_{cr}(n_{1'} - n_{2'}), \tag{4}$$

where $w_{cr} = W_{21',2'1}^{cr}(n_2 + n_{2'})/N_0$. In the high-temperature approximation ($h\nu_{11'} \ll kT$) we have

$$\frac{n_2+n_{2'}}{N_0} \approx \frac{N_2+N_{2'}}{N_0},$$

where N_i is the population of the i-th level at thermodynamic equilibrium, and then w_{cr} in (4) takes the form

$$w_{cr}' \approx w_{21,'2'1} \frac{N_2+N_{2'}}{N_0} g(\Delta\nu_{SI}^{(i)}, \Delta\nu_{cr}) \equiv w_n^{eff}, \qquad (5)$$

where $(N_2 + N_{2'})/N_0$ determines the fraction of the spins that are directly saturated by the microwave field. Since the states $2 - 1$ and $2' - 1'$ differ only in their nuclear quantum number, it follows that the transitions (5) (which are generated by the electronic CRT) are best interpreted as effective spin-lattice nuclear transitions of the type w_n.[1)]

A theoretical study of the saturation of ENDOR signals in a four-level system, with allowance for all the possible relaxation and induced transitions, was carried out earlier[12]. The same study yielded explicit expressions for the longitudinal relaxation time T_{1n} of the nuclei, in terms of the probabilities of the various spin-lattice transitions. Since the electronic CRT could be reduced to effective spin-lattice transitions, the results of[12] can be directly applied to our case. According to[12] (see also[13]), the dependence of the ENDOR signal intensity on the rf-field intensity is represented in the form

$$\delta = K\frac{y^2}{1+y^2}, \qquad (6)$$

where K is a quantity that depends on the power and the frequency of the microwave field, $y^2 = 2T_{1n}W$ is the parameter of the saturation of the ENDOR signal by the rf field, and W is the probability of the induced rf transition. At resonance[13] we have

$$y^2 = \frac{1}{4}\gamma_n^2 H_2^2 \left(1 - M\frac{\Delta\nu_{SI}^{(i)}}{\nu_n^{(i)}}\right)^2 r_m^2 T_{1n} T_{2n},$$

where γ_n is the gyromagnetic ratio of the resonating nuclei, T_{2n} is their transverse relaxation time, and $r_m = [(I + m)(I - m + 1)]^{1/2}$, where m is the projection of I on H.

Plots of δ against H_2, in accord with (6), are shown in Fig. 2 by solid lines. The theoretical relations are tied in with the experimental data at a single point. The values of $(T_{1n}T_{2n})^{1/2}$ for the various curves were determined in accordance with this point at $y^2 = 1$ and $\delta = 0.5\,\delta_{max}$. According to[14], $T_{2n} = 2.6 \times 10^{-5}$ and 1.1×10^{-5} sec for the nuclei Li^7 and F^{19}, respectively (these are close to the values of T_{2n} determined from the ENDOR line widths). From curves 1 and 2 of Fig. 2 we find that the value of T_{1n} determined from curve 1 is approximately 1.7 times larger than that determined from curve 2. The time T_{1n} determined from curve 1 is $T_{1n} \approx 4 \times 10^{-4}$ sec. The times T_{1n} for close values of $\Delta\nu_{SI}^{(i)}$ are approximately equal for the nuclei Li^7 and F^{19}. From curves 1 and 3 of Fig. 2 we find that the T_{1n} of the nuclei in sample I is approximately three times as large as in sample II.

The dependence of $\Delta\nu$ on H_2 (at low microwave-field levels) can be represented in the form (see[12]) $\Delta\nu \approx \Delta\nu_0(1 + y^2)^{1/2}$. The longitudinal relaxation time T_{1n} is 1.3 times larger for curve 1 than for curve 2. The experimentally observed broadening of the ENDOR lines is weaker than would follow from the formula $\Delta\nu \approx \Delta\nu_0(1 + y^2)^{1/2}$. The reason seems to be that $\Delta\nu_0$ is in part due to inhomogeneously broadening mechanisms[13].

An analysis of the quantity T_{1n} expressed in terms of the probabilities of different spin-lattice transitions[2)] shows that the experimentally obtained values of the T_{1n} of the nuclei and the dependences of T_{1n} on $\Delta\nu_{SI}^{(i)}$ (i.e., on the HFI constants and on the orientation), on the F-center concentration, and on the crystal temperature cannot be attributed to the nuclear-relaxation mechanism described in[1,2,4].

Replacing the probability w_n in the expression for T_{1n}[12] by the quantity w_n^{eff} introduced by us, and assuming that the processes w_s and w_n^{eff} predominate over the processes w_x and w_x' (the processes w_s, w_n, w_x, and w_x' are determined by the customary selection rules, see, e.g.,[4,12]), we obtain

$$T_{1n} = (2w_n^{eff} + w_s)[2w_n^{eff}(2w_n^{eff} + 2w_s)]^{-1}.$$

If $w_s \gg w_n^{eff}$, then

$$(T_{1n})^{-1} \approx 4w_n^{eff} = 4w_{21',2'1}\frac{N_2+N_{2'}}{N_0} g(\Delta\nu_{SI}^{(i)}, \Delta\nu_{cr}). \qquad (7)$$

With increasing $\Delta\nu_{SI}^{(i)}$, of the nuclei, the factor due to the form function in (7) decreases, i.e., T_{1n} is different for nuclei with different $\Delta\nu_{SI}^{(i)}$. This makes it possible, in favorable cases, to investigate the CRT probability function experimentally.

Starting from (7), we can explain the experimentally observed dependence of T_{1n} on the $\Delta\nu_{SI}^{(i)}$ of the nuclei, on the F-center concentration, and on the crystal temperature. Allowing for the rather crude character of the approach developed here, expression (7) cannot claim to provide an exact quantitative description of the experimental data. However, an estimate of the quantity $w_{21',2'1}$ in accordance with the formulas of[10] (with allowance for the fact that the investigated system is magnetically dilute) and of the value of $(N_2 + N_{2'})/N_0$ starting from the assumption that the EPR line is formed mainly by the interaction with nuclei of the first two coordination spheres yields the required order of magnitude of T_{1n}.

We note that, according to the described mechanism, paramagnetic centers whose local fields are different (owing to the HFI with the nuclei) participate in the CRT, and the electron-spin system receives not the Zeeman energy $h\nu_n^{(i)}$ and not the total energy of the nuclei $h|\nu_n^{(i)} - M\Delta\nu_{SI}^{(i)}|$, but the HFI energy, which in our experiments is much lower than the Zeeman energy. An important factor is the microwave saturation of the transitions, since it is necessary to have spin diffusion along the EPR line.

For the nuclei of the first two coordination spheres we have $\Delta\nu_{SI}^{(i)} \gg \Delta\nu_{cr}$, and therefore the proposed mechanism, according to (7), makes a negligible contribution to the relaxation of these nuclei, which is apparently due to one of the mechanisms described by Khutsishvili[1] and by Pines, Bardeen, and Schlichter[4]. We note that the effectiveness of these mechanisms increases sharply with increasing HFI constants, in contrast to the proposed mechanism, whose efficiency decreases with increasing $\Delta\nu_{SI}^{(i)}$.

It should be noted that each separately registered group of nuclei of close coordination spheres of the paramagnetic center can, in principle, relax by a different mechanism. The distinguishing features of the proposed relaxation mechanism are the following. Since identical nuclei of the same coordination sphere, located near paramagnetic centers with $M = +\frac{1}{2}$ and $M = -\frac{1}{2}$, constitute two different (separately registered) groups of nuclei, the considered CRT can ensure relaxation of each of these two groups of nuclei. Thus, if the 2-2′ transition is saturated (see Fig. 4), then a nonequilibrium magnetization is produced along H in each of these two groups of nuclei, and this magnetization tends to attain equilibrium by means of the described mechanism. In each individual act of cross relaxation (without reorientation of the nuclear spins), the projection of the magnetization on the field H changes in both groups of nuclei. The change of magnetization of each of the two groups of nuclei is such that their total magnetization remains unchanged. If we observe one group of nuclei (for example, the group with $M = +\frac{1}{2}$), then a nucleus "goes away" from this group with one orientation of the nuclear spin in the case of the described cross-relaxation transition (it begins to resonate at a different frequency) and "arrives" with the opposite orientation, i.e., we have a change of magnetization in the observed group, and consequently relaxation.

In our experiments we did not record any nuclei resonating at the Larmor frequency. It is obvious that this mechanism is not effective for these nuclei, for if $\Delta\nu_{SI}^{(i)} \approx 0$, then the transitions 1-1′ and 2-2′ are simultaneously and equally saturated by the microwave field, and $(dn_2/dt)_{cr}$ from (2) is equal to zero (i.e., the cross relaxation is frozen[15]). In addition, the CRT without reorientation of the nuclear spins can ensure relaxation only for those nuclei whose ENDOR lines are registered separately at the frequencies (1).

The induced rf transitions that cause the ENDOR spectrum operate between the same levels as the transitions (5). The enhancement of w_n of the process leads to a weakening of the ENDOR lines, inasmuch as the population excess between the nuclear sublevels, produced by the saturation of the microwave transitions, is thereby decreased. Since the probability w_n^{eff} increases with decreasing $\Delta\nu_{SI}^{(i)}$, an equal degree of saturation of the ENDOR lines with different $\Delta\nu_{SI}^{(i)}$ will be reached at different H_2. This causes the ratio of the intensities of the different ENDOR lines to depend on the value of H_2 at which they are registered, see Fig. 1.

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1)The electronic CRT were first reduced to the transitions w_n^{eff} in [11]. For level 2, the term due to the nuclear spin-lattice transitions w_n in the equations for the populations takes the form $w_n[n_1-n_2)-(N_1-N_2)]$. Since the microwave transition 2 – 2′ is saturated, the population difference (n_1-n_2) in our case is of the order of $(N_{2'}-N_2)$, with $|N_{2'}-N_2| \gg |N_1-N_2|$. We can therefore neglect N_1-N_2 in comparison with n_1-n_2.

2)A detailed expression for T_{1n} is given in [12] (formula (17)); it is too cumbersome to write out here.

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24