CONCLUSION

It is shown in this paper that the total cross section for the capture of an electron by a positive center, with transfer of the excess energy to acoustic phonons, under conditions when the quasi-classical analysis is valid, is described by formula (1). It differs from Lax's well known expression for the cross section in the fact that it is larger than the latter by a factor $2kT/ms^2$ and is inversely proportional to the third power of the temperature and not to the fourth power as in Lax's formula.

We have shown that the total recombination cross section is much easier to calculate by Pitaevskiĭ's method than by Lax's method (supplemented by the requirement that the probability of the electronic transitions be correctly averaged). However, Lax's method has the advantage that it makes it easy to obtain the cross section for capture of an electron with a fixed energy E_0 by a recombination center, if the sticking function is known

$$\sigma(\xi)=\int_0^\infty \sigma(\xi,\eta)P(\eta)\,d\eta$$

$$=\frac{\sigma_1}{\xi}\int_0^\infty \frac{P(\eta)(\xi+\eta)^2 d\eta}{\{[1+(\xi+\eta)/4]^2-\xi\}^3\{1-\exp[-(\xi+\eta)/\gamma]\}}, \tag{32}$$

where ξ, η and γ are defined in (23). For $\xi \gg 1$ the main contribution to the cross section $\sigma(\xi)$ is made by captures on levels with dimensionless binding energy $\eta \sim \xi \gg 1$, so that expression (31) can be used for the sticking function and we get

$$\begin{aligned}\sigma(\xi)&=\frac{2}{3}\frac{4^4\sigma_1}{\xi^3\gamma}, \quad 1\ll\xi\ll\gamma,\\ \sigma(\xi)&=\frac{4^6}{3}\frac{\sigma_1}{\xi^4}, \quad \xi\gg\gamma.\end{aligned} \tag{33}$$

It is seen from this formula that the differential capture cross section increases rapidly with decreasing ξ, and this explains the decisive role played by capture of electrons with low energies in the recombination process.

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New effect in electron-nuclear double resonance with distant nuclei

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Anomalously intense ENDOR signals due to polarization of the lattice nuclei ("Larmor" ENDOR) are observed in LiF crystals with relatively low F-center concentrations ($n\sim 2\times10^{17}$ cm^{-3}) at the Larmor frequency of the lattice nuclei. The dependences of the ENDOR signal intensity on the microwave field strength and on the mismatch ($H-H_0$) (H_0 is the magnetic field strength corresponding to the center of the ESR line) are studied at various temperatures and concentrations of the paramagnetic centers. It is found that the dynamic behavior of the Larmor ENDOR is the opposite of that of the "distant" ENDOR described in the literature, in which signals at the Larmor frequency of the lattice nuclei are also observed. Larmor ENDOR is observed in samples with relatively low concentrations of paramagnetic centers and is maximal at the center of the ESR line. The ENDOR mechanism is not the same for distant and near nuclei. It is shown that lattice nuclear polarization required for the observation of Larmor ENDOR is not connected with dipole–dipole pool effects and can be ascribed to relaxation processes or to saturation of forbidden microwave transitions. It is important that Larmor ENDOR is observed in the presence of regions with nonequilibrium nuclear polarization in the sample even if there is no net polarization. It is found that the existence of Larmor ENDOR may be regarded as experimental proof that the lattice nuclei relax via a paramagnetic impurity.

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The study of the dynamic laws and mechanisms governing the production of electron-nuclear double resonance (ENDOR) signals yields not only detailed information of the physical processes occurring in bound electron-nuclear systems, but also contributes to a wider and more successful application of this method. The most investigated ENDOR mechanisms are the mechanism connected with the effective decrease $T_1 \to T_1^{\rm eff}$ of the time of the spin-lattice relaxation by a radio-frequency (RF) field,[1,2] and the method of "distant" ENDOR.[2–4] Mechanisms of "negative" ENDOR,[5,6] ENDOR due to shift of the ESR line,[7] and due to re-

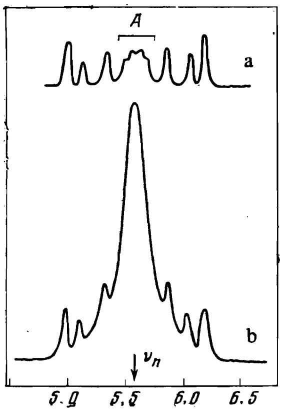

FIG. 1. Form of the ENDOR spectrum from nuclei of the third, fifth, and more distant lithium F-center coordination spheres in the absence of the Larmor ENDOR effect (Fig. a); b) the same spectrum in the presence of the Larmor ENDOR. The abscissas show the frequency of the RF field in MHz. H lies in the (001) plane and makes an angle 28° with the [100] axis.

orientation of spin packets[2,8,9] have also been described.

Each of these mechanisms is connected with certain physical processes that occur in the investigated object. In turn, different physical processes lead to unequal dynamic regularities, which serve as the experimental criteria for the different ENDOR mechanisms. We present below the results of a study of dynamic regularities and the mechanism for the onset of anomalously intense ENDOR signals, observed by us at the Larmor frequencies of the lattice nuclei in the crystals LiF and SiO_2.

EXPERIMENT

The measurements were performed with a superheterodyne ENDOR spectrometer operating in the three-centimeter band[10] (ν_{micr} = 9447 MHz). The main objects of the investigation were the F centers in LiF crystals. The F centers were obtained by bombardment with γ rays from a cobalt gun, and their concentration was determined from optical measurements. The experiments were performed at temperatures 20, 77, and 300 °K. We investigated the ENDOR signals from the nuclei of coordination spheres I–VIII, and also signals observed at an RF field frequency equal to the Larmor frequency of the lattice nuclei, $\nu_{RF} = \nu_n$.

In samples with relatively low F-center concentrations, $n \sim 2\times10^{17}$ cm^{-3}, we have observed at T = 20 and 77 °K an effect wherein the intensity of the ENDOR signal at the Larmor frequency of the lattice nuclei increased sharply (Fig. 1). The spectrum shown in Fig. 1a was observed in samples with appreciable F-center concentrations, $n \sim 10^{18}$ cm^{-3}, at any crystal temperature, and also in samples with low F-center concentration at T = 300 °K. The spectrum shown in Fig. 1b was observed in samples with low F-center concentration at T = 77 and 20 °K. The anomalous ENDOR signal produced at the Larmor frequency of the lattice nuclei (see Fig. 1b) will be called the "Larmor" signal.

We have investigated the intensities δ of the ENDOR signals as functions of the microwave field intensity H_1 for the already indicated group of nuclei in the presence and in the absence of Larmor ENDOR. In both cases, the saturation curves of the nuclei of the coordination spheres I–VIII are close to the analogous plots described in[11]. In the presence of Larmor ENDOR, the saturation curve is different only for the ENDOR at $\nu_{RF} = \nu_n$.

For all other ENDOR signals, the variations of the temperature or of the concentration lead only to a shift of the saturation curves without a significant change in their shape. Figure 2 shows the saturation curves for certain nuclei and illustrates the indicated effect.

A study of the dependence of δ on the mismatch $|H - H_0|$ (H_0 is the magnetic field corresponding to the center of the ESR line) has shown that the intensities of the ENDOR signals are maximal at $H = H_0$ and decrease with increasing $|H - H_0|$. In the case of the Larmor ENDOR the dependence of δ on $|H - H_0|$ is somewhat sharper than for ordinary ENDOR, for which these dependences duplicate approximately the course of the ESR line.[11]

The Larmor ENDOR effects were observed by us, not only for Li^7 and F^{19} nuclei in LiF crystals, but also at $T \approx 20$ °K for Si^{29} nuclei in quartz crystals containing Ti^{3+}(Li) and Al–O$^-$ centers (the ESR spectra of these centers were described by Rinneberg and Weil[12] and by O'Brien[13]). In these objects, ENDOR signals were recorded from the nuclei Li^7 and Si^{29} (Ti^{3+}(Li) center) and from Al^{27} and Si^{29} (Al–O$^-$ center), the ENDOR signals from Si^{29} being observed only at the Larmor frequency of these nuclei. The dynamic regularities of the Larmor ENDOR in quartz are close to the analogous regularities for the LiF crystals.

In the described experiments, the ENDOR signal was

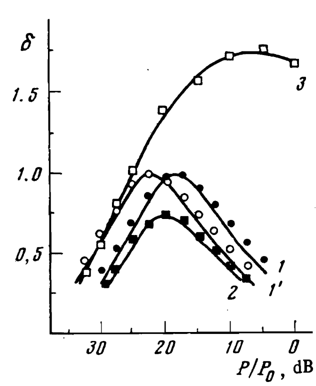

FIG. 2. The saturation curves 1 and 2 pertain to the ENDOR from the nuclei of sphere III and to the ENDOR at $\nu_{RF} = \nu_n(Li^7)$ in a sample with $n \sim 10^{18}$ cm^{-3}, T = 77 °K (case of absence of Larmor ENDOR). Curves 1′ and 3 correspond to ENDOR of sphere III and to ENDOR at $\nu_{RF} = \nu_n(Li^7)$ in a sample with $n \sim 2\times10^{17}$ cm^{-3}, T = 77 °K (case of presence of Larmor ENDOR). The transition to T = 20 °K did not lead to a growth of the effect of the Larmor ENDOR. The intensities of the signals for curves 1 and 1′ were normalized to unity. The abscissas represent the attenuation of the microwave power field in decibels. The zero decibel point corresponds to a power $P \approx 6$ MW.

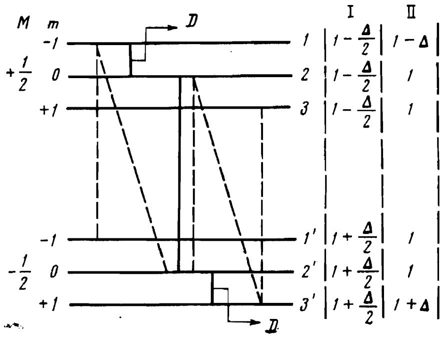

FIG. 3. Energy level scheme of the considered model. The vertical dashed lines correspond to w_S relaxation, and the inclined lines correspond to w_X relaxation, while the solid line is the saturating microwave signal, and D indicates the diffusion of the polarization to the nuclei of the lattice. The numbers 1, 2, etc. label the levels. In column I are indicated the relative populations of the levels for thermodynamic equilibrium, while II shows the populations in the case of saturation of the 2–2′ transition. M and m are respectively the magnetic quantum numbers of the electron and of the nucleus.

due to the increase of the imaginary part of the magnetic susceptibility under the influence of the RF field. A study of KBr crystals with different F-center concentrations has shown that there are no manifestations of Larmor ENDOR whatever in these crystals.

DISCUSSION OF EXPERIMENT

It is known that the F centers in LiF constitute a system in which the cross relaxation is quite weak. In this case we can obtain for the intensities of the ENDOR signals from nuclei of different coordination spheres, in the $T_1 \to T_1^{\mathrm{eff}}$ mechanism[11]

$$\delta_f(H_1) \sim \left[\left(\frac{x}{1+\alpha_f x}\right)^{1/2} U_f' - \left(\frac{x}{1+x}\right)^{1/2} U_f\right], \tag{1}$$

where $x=\gamma^2 H_1^2 T_1 T_2$, here $T_2=(\Delta\omega_L)^{-1}$ is the time of the spin–spin relaxation $\alpha_f = T_1^{\mathrm{eff}}(T_1)^{-1}$ (T_1^{eff} is the effective time of the spin-lattice relaxation in the presence of a RF field, U_f is the convolution of a Gaussian and Lorentzian with respective widths $\Delta\omega_f$ and $\Delta\omega_L(1+x)^{1/2}$. For U_f' the width of the Lorentzian is $\Delta\omega_L(1+\alpha_f x)^{1/2}$. The quantity $\Delta\omega_f$ is determined by the hyperfine interaction (HFI) of the F center with the nuclei having HFI constants that are smaller than the resonant (f-th) nuclei.[11] $\Delta\omega_f$ is different for different coordination spheres.

At $\Delta\omega_f \ll \Delta\omega_L$ (as is the case for nuclei with small HFI constants) we obtain from (1)

$$\delta(H_1) \sim \left[\frac{\sqrt{x}}{1+\alpha x} - \frac{\sqrt{x}}{1+x}\right], \tag{2}$$

Expression (1) describes satisfactorily the saturation curves for the nuclei of coordination spheres I–VIII.[11] The theoretical relations for sphere III ($\Delta\omega_L/\Delta\omega_f \sim 1$, $\alpha=0.9$) are shown in Fig. 2 by solid lines (curves 1 and 1′, the shift of which is due to the change of T_2). For ordinary ENDOR at $\nu_{\mathrm{RF}}=\nu_n$, the saturation curve is satisfactorily described by expression (2) (curve 2 in Fig. 2). It follows therefore that in this case for ENDOR at $\nu_{\mathrm{RF}}=\nu_n$ (as well as for ENDOR on the remaining nuclei) the mechanism $T_1 \to T_1^{\mathrm{eff}}$ is realized, and it can be regarded as ENDOR from nuclei of distant spheres, the spectra of which are not resolved (the experiments[14] confirmed directly the $T_1 \to T_1^{\mathrm{eff}}$ mechanism for nuclei of coordination spheres I–VIII). However, curve 3 of Fig. 2 deviates strongly from expressions (1) and (2), i.e., the Larmor ENDOR cannot be regarded as ordinary ENDOR from nuclei of distant coordination spheres whose spectra are not resolved.

The very fact that an intense ENDOR signal exists at the Larmor frequency indicates that for a certain group of nuclei (the interaction of which with the F center is weak or negligible) there exists an appreciable polarization, since the necessary condition for the observation of the ENDOR is an appreciable population difference between the energy levels that absorb the RF quanta.[2]

The distant nuclei, which have negligible HFI, can be polarized by diffusion of the polarization[15,16] from intermediate nuclei having noticable HFI. The polarization-diffusion processes are analogous to spin diffusion in the case of nuclear relaxation via a paramagnetic impurity. Thus, if the HFI constants of the polarized (intermediate) nuclei do not greatly exceed the width of the ENDOR lines (section A in Fig. 1a), and if processes of spin diffusion of nuclei are effective in the investigated object, then the considered polarization will diffuse to the bulk of the target nuclei. In turn, the presence of Larmor ENDOR (and accordingly of the diffusion processes) can serve as an experimental criterion that the lattice nuclei relax via a paramagnetic impurity. The size of the region over which the polarization extends is determined by the competition of the diffusion and nuclear-relaxation processes.

There exist various mechanisms for nuclear polarization.[17,18] For the mechanisms connected with the dipole–dipole pool (DDP) of the electron spins,[19,17,4] there is no polarization[1)] if $H=H_0$. The polarization of the intermediate nuclei, which is produced in our experiments upon saturation of the microwave transitions at the center of the ESR line, can be connected either with forbidden microwave transitions or with relaxation processes.

Let us explain the relaxation variant of the polarization with the aid of a model consisting of an electron and a nucleus with spin $I=1$ (see Fig. 3), in which transitions w_s, w_x, w_x', and w_n are possible.[20,21] Saturation with a microwave field of an allowed 2–2′ transition at a favorable ratio of their relaxation probabilities can lead to polarization of these nuclei. For example, at $w_x \gg w_x'$ and $w_x \gg w_n$ there will be an appreciable population difference between levels 1–2 and 2′–3′ (Fig. 3), so that the polarization of the nuclei will be of the order of $h\nu_{\mathrm{micr}}/3kT$.[2] The condition $w_x \neq w_x'$ (which is necessary for polarization) is satisfied most obviously if the isotropic HFI predominates.[20,21] The nonmonotonic decrease of the wave function of the F center at the nuclei of the remote spheres[22] can ensure $w_x > w_x'$ for these nuclei.

In addition, in the case of saturation of a central spin packet with resonant frequency ν_0, saturation is possible via forbidden microwave transitions of the spin packets with resonant frequencies $\nu_0+\nu_n$ and $\nu_0-\nu_n$.[17,18] Therefore polarizations of opposite signs can be produced around the paramagnetic centers of the packets $\nu_0+\nu_n$ and $\nu_0-\nu_n$.[17] If $H=H_0$, then there is no net polarization. However, if regions in which the polarization is appreciable actually exist in the sample, then the depolarization of the nuclei by the RF field, independently of the sign of the polarization, will lead to a growth of the imaginary part of the magnetic susceptibility. Therefore the intensity of the Larmor ENDOR will be largest at $H=H_0$, when the sum of the polarizations in different regions of the sample is maximal in absolute value. For LiF crystals this variant of the polarization seems the most probable. However, it is difficult to separate the considered polarization mechanisms reliably within the limits of ENDOR experiments.

With increasing concentration of the paramagnetic centers, for nuclei responsible for the polarization, the role of the w_n process can be played by the effective processes w_n^{eff} connected with cross relaxation of the electron spin.[23] If $w_n > w_x$ and $w_x' > w_x$, then there is no polarization.[18] The change of the crystal temperature, and also of the concentration of the centers, can change the ratio of the diffusion and nuclear-relaxation processes, and this influences the picture of the polarization of the nuclei in the investigated object.[17]

It follows from the described dynamic regularities that the Larmor ENDOR differs qualitatively from the ENDOR mechanisms considered in the literature. It is important to note that with respect to its regularities it is the opposite of distant ENDOR,[2-4] which is observed also at the Larmor frequency of the lattice nuclei (the fact that the described phenomenon does not agree with the mechanisms of[5,7,9] is obvious). For example, in distant ENDOR the effects are maximal in samples with large concentration of the paramagnetic centers, while the ENDOR mechanisms at nuclei with different hfs constants is the same, and the very effect is observed on the slopes of the ESR line and is absent at $H=H_0$.

KBr (in contrast to LiF) is a crystal whose nuclear relaxation is not connected with F centers, but is due to quadrupole interactions.[16] The ineffectiveness of the spin-diffusion of the nuclei in this crystal does not make it possible to observe Larmor ENDOR in it.

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