as a constant source of supply.

The authors are grateful to V. I. Magalyas for developing the experimental diodes and to Yu. V. Romanov for taking part in the measurements.

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INFLUENCE OF EXCHANGE NARROWING OF EPR ON THE DYNAMIC POLARIZATION OF NUCLEI

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Submitted 21 June 1967
ZhETF Pis'ma 6, No. 5, 665-667 (1 September 1967)

It is shown in a number of papers [1], by means of a quantum-statistical analysis, that dipole-dipole (d-d) interaction between the electron spins exerts a strong influence on the dynamic polarization of nuclei (DPN). In the simple theory the DPN is obtained by saturation of forbidden resonances (FR) at frequencies $\omega^{\pm} = \omega_s \pm \omega_z$, so that the frequency spacing between the polarization maxima (of opposite signs) is equal to $D = 2\omega_I$ (ω_s and ω_I are the frequencies of the electron and nuclear resonances). In the rigorous theory of DPN [1] D can have values smaller than $2\omega_I$. It has been recently established by experiment [2] that D is much smaller than $2\omega_I$ in certain substances containing free radicals, and other anomalies have also been observed, which cannot be understood if only d-d interaction between electrons is taken into account. We show in this note that simultaneous allowance for exchange interaction (H_{ex}) and d-d interaction between the electrons improves greatly the agreement between theory and experiment.

Let us consider the case of strong fields, when the Zeeman electron energy H_z is much higher than their exchange and d-d energies, and the influence of the nonsecular part of the d-d interaction can be neglected. Under these conditions one should choose as a separate subsystem a system with Hamiltonian $H_e = H_{ex} + H_d$, which we shall call the exchange reservoir (ER). H_d is the secular part of the d-d interaction. The problem under consideration is equivalent mathematically to the problems solved in [1]. In the case of fast spin diffusion, the nuclear Zeeman subsystem (NZS) is characterized by a single reciprocal temperature β_I, which is defined in the stationary state by the formula

$$\beta_I = \frac{\beta_L}{2W_0(\Delta)\,T_s(\alpha\omega_e^2 + \Delta^2) + \alpha\omega_e^2}\left\{2\omega_s W_0(\Delta)\,T_s\,\Delta + \frac{\omega_s}{\omega_I}\,\frac{\alpha\omega_e^2\,[W(\omega^-) - W(\omega^+)]}{1/T_I + W(\omega^-) + W(\omega^+)}\right\}. \quad (1)$$

Here ω_e is the frequency corresponding to the interaction H_e, $\alpha = T_s/T_e$, where T_s and T_e are the spin-lattice relaxation times of the electronic Zeeman subsystem and the ER. T_I is the time of relaxation of the NZS to the ER, $\Delta = \omega_s - \omega$, ω is the frequency of the alternating magnetic field, $W_o(\Delta)$ is the probability of the ordinary paramagnetic resonance, $W(\omega^\pm)$ are the probabilities of the forbidden resonances, and β_L is the reciprocal lattice temperature. At sufficiently high impurity concentrations, $H_{ex} >> H_d$ and the EPR line becomes narrower [3], the forbidden transitions (FT) become broader [4], and the rate of the NZS → ER relaxation increases. It is clear from the foregoing that the FT saturation is greatly hindered; with this, the saturation of the ordinary resonance is facilitated as ω approaches the center of the EPR line. Neglecting in (1) the terms connected with the FT and including by the same token only the effect due to the NZS → ER relaxation, we obtain

$$\beta_I = \beta_L \frac{2\omega_s W_o(\Delta) T_s \Delta}{2W_o(\Delta) T_s (a\omega_e^2 + \Delta^2) + a\omega_e^2} \qquad (2)$$

The quantity $|\beta_I|$ has maxima at the frequencies

$$\Delta_\pm = \pm\sqrt{\frac{2W_o(0) T_s \Gamma^2 \cdot a\omega_e^2}{2W_o(0) T_s \Gamma^2 + a\omega_e^2}},$$

where Γ is the EPR line width with allowance for the exchange narrowing. At large values of H_{ex} the width Γ is small, $\Delta_\pm \approx \pm\sqrt{2W_o(0)T_s}\,\Gamma$ and

$$D \simeq 2\sqrt{2W_o(0) T_s}\;\Gamma . \qquad (3)$$

The maximum value of $|\beta_I|$ is found from (2) to be

$$|\beta_I|_{max} \sim \frac{\omega_s}{\sqrt{a}\,\omega_e}\sqrt{2W_o(0) T_s \frac{\Gamma^2}{a\omega_e^2}} . \qquad (4)$$

Recognizing that Γ decreases with increasing spin concentration [3], expression (3), in contradiction to the conclusions of [1], agrees with the experiments [2] in which a tendency was observed for D to decrease with increasing concentration. It should be noted that in our analysis the forbidden resonances do not saturate at the frequencies $\Delta_\pm$ corresponding to the polarization maxima. The parameter of the EPR saturation at these frequencies is small, $S = 2W_o(\Delta_\pm)T_s \approx 1$. These conclusions agree also with [2], where it is noted that at the frequencies $\Delta_\pm$ there should be no saturation of either the allowed or forbidden resonances.

In conclusion, the authors thank G. R. Khutsishvili for discussions.

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