Electron-nuclear double resonance in a nonuniform magnetic field

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An electron-nuclear double resonance (ENDOR) in a nonuniform magnetic field has been studied theoretically and experimentally for the first time. Expressions for the ENDOR signal are derived. In the case of broad ESR lines and narrow NMR lines, the shape of the signal is shown to reproduce the distribution of paramagnetic centers over the sample. If the ESR lines are instead narrow, there is spatial focusing of the resonance. Experiments were carried out with LiF crystals containing *F*-centers. A sample with a uniform distribution of *F*-centers and samples with diamagnetic "holes" of various sizes were studied. These holes, which are not seen in the ESR, are quite evident in the ENDOR spectrum. The ENDOR spectrum depends in an unusual way on the "landing site" on the ESR line, because signals from parts of the sample where the magnetic field deviates from the resonant field are attenuated. The observation of ENDOR in a nonuniform magnetic field opens up new opportunities for studying cross relaxation, spatial diffusion of nuclear polarization, and nuclear relaxation through paramagnetic centers. ENDOR holds promise for subsurface imaging. It is shown, in particular, that ENDOR subsurface imaging would be most effective for just these objects for which ESR subsurface imaging fails. In terms of spatial resolution, ENDOR subsurface imaging approaches NMR subsurface imaging. In addition, it provides information on paramagnetic effects which are inaccessible by the NMR method.

INTRODUCTION

Research on magnetic resonances in nonuniform fields has spawned a new and rapidly developing field of science: magnetic-resonance subsurface imaging or tomography, whose goal is to obtain information on the three-dimensional structures of objects. The NMR method has been most successful in this field (see, for example, the review by Atsarkin *et al.*[1]). An effort has also been undertaken to use ESR[2] for these purposes; ESR has proved effective in studying solids.

It is worthwhile to examine the possible use of the electron-nuclear double resonance (ENDOR)[3,4] for subsurface imaging. This effect is known to combine the high resolution of NMR with the sensitivity of ESR.

In the present paper we report a theoretical and experimental study of ENDOR in a nonuniform magnetic field. We derive and analyze expressions describing the ENDOR signal. We report an experimental test. We discuss the advantages of ENDOR subsurface imaging and its possible fields of application.

THEORY

In a nonuniform magnetic field $H(x,y,z)$, which we write as the sum of a uniform field H and an increment $\Delta H(x,y,z)$ which varies along the coordinates, the ESR signal is

$$I(H)=c_1\int\limits_v \rho(x,y,z)g[H-(H_0-\Delta H(x,y,z))]dx\,dy\,dz, \quad (1)$$

where the function $\rho(x,y,z)$ describes the distribution of paramagnetic centers over the sample volume v, the function $g(H-H_0)$ describes the ESR lineshape in a uniform field, H_0 is the resonant field, and the quantity c with a number subscript is a dimensional proportionality factor. The direction of the nonuniform magnetic field is assumed to be the same as that of the uniform field at all points in space. If the ESR is detected by scanning the field H in time and plotting its values (measured by a pickup of some sort) along the abscissa, the value of $\Delta H(x,y,z)$ on this scale will characterize the shift of the resonant field for centers at various points in the sample. In expression (1), H and $\Delta H(x,y,z)$ are assumed to be independent as H is varied over the ESR line. If this is not the case, we should replace $\Delta H(x,y,z)$ in (1) by $\Delta H(H,x,y,z)$.

The ENDOR signal is the change in the amplitude of the ESR signal at the spectral point $H=H^*$ (the point of the "landing" on the ESR line) when the frequency ν of the rf field applied to the sample becomes equal to the resonant frequency ν_0 of the nuclear transition associated with the ESR. The NMR lineshape function corresponding to this nuclear transition is denoted by $g_n(\nu-\nu_0)$. According to Refs. 5–7, for steady-state ENDOR, to which we restrict the present analysis, the H dependence of the absorption signal in a nonuniform magnetic field reproduces the ESR lineshape, while the ν dependence reproduces the NMR lineshape. The ENDOR signal in a nonuniform magnetic field can then be described by

$$I(\nu)=c_2\int\limits_v \rho(x,y,z)g[H^*-(H_0-\Delta H(x,y,z))]$$
$$\times g_n[\nu-(\nu_0+\gamma\Delta H(x,y,z))]dx\,dy\,dz. \quad (2)$$

Here γ is the nuclear gyromagnetic ratio, and $\nu_0=\gamma H^*-MA$ (M is the quantum number determined by the projection of the electron spin onto the magnetic field,

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and A is the hyperfine constant). For simplicity, we have assumed in (1) and (2) that the amplitudes of the microwave and rf fields remain constant over the sample volume.

In experiments with nonuniform fields, the magnetic field usually has a one-dimensional gradient (along the z axis, for example), and ΔH is usually a linear function of a coordinate. In this case, expression (2) becomes

$$I(\nu)=c_3\int_0^l \rho(z)g[H^*-(H_0-kz)]g_n[\nu-(\nu_0+\gamma kz)]dz, \qquad (3)$$

where l is the dimension of the sample along the z axis, whose origin is placed at one end of the sample; $k=dH(z)dz$; c_3 incorporates the intensity of the signal from a thin layer of the sample of thickness dz, perpendicular to the z axis; and $\rho(z)$ reflects the relative change in the intensity of these layers along z. In the case in which the distribution of paramagnetic centers is uniform as a function of x and y, the function $\rho(z)$ is the distribution function of these centers as a function of z in the sample.

If the width of the ESR line in a nonuniform magnetic field δH is significantly greater than the maximum change in the field over the sample, i.e., if the condition

$$\delta H\gg kl \qquad (4)$$

holds, then for ordinary resonance lines (of smooth shape) we have

$$g[H^*-(H_0-kz)]\approx g(H^*-H_0),$$

and expression (3) becomes

$$I(\nu)\approx c_4(H^*)\int_0^l \rho(z)g_n[\nu-(\nu_0+\gamma kz)]dz. \qquad (5)$$

Expression (5) is precisely the same in form as the expression which is used to describe NMR in a nonuniform magnetic field, differing only in the meaning of the function $\rho(z)$. In the case of narrow NMR lines ($\delta\nu$ is the width of the line in a uniform field), which satisfy the conditions

$$(\gamma k)^{-1}\delta\nu\ll l, \qquad [d\rho(z)/dz](\gamma k)^{-1}\delta\nu\ll\rho(z), \qquad (6)$$

the measured signal,

$$I(\nu)\approx c_5(H^*)\rho[z(\nu)], \qquad (7)$$

is a direct plot of the function $\rho(z)$ if a z scale is plotted along the abscissa in place of ν in accordance with $z=(\gamma k)^{-1}(\nu-\nu_0)$. The coefficient $c_5(H^*)$, which determines the overall intensity of this signal, depends on the "landing" site on the ESR line. It is zero if we are outside the ESR line.

In the other limiting case (of narrow ESR lines), in which we have

$$k^{-1}\delta H\ll l, \qquad [d(\rho(z)g_n(z))/dz]k^{-1}\delta H\ll\rho(z)g_n(z), \quad (8)$$

the ENDOR signal will be detected only from the point $z^*=k^{-1}(H_0-H^*)$ in the sample and will have the shape of an isolated MNR line:

$$I(\nu)\approx c_6\rho(z^*)g_n[\nu-(\nu_0+\gamma kz^*)]. \qquad (9)$$

In this case, the ENDOR is focused at the point z^* in the sample. By varying H^*, we can obtain a set of signals (9) from different points in the sample.

Analysis of expression (3) shows that for intermediate values of the widths of the resonance lines ($\delta H\sim kl, \delta\nu\sim\gamma kl$), there will be prominent signals in the $I(\nu)$ spectrum from a part of the sample of size $\Delta z\sim k^{-1}\delta H$, where the magnetic field is close to the resonant value. The signals from other regions will be suppressed, to an extent which increases with the deviation of these regions from resonance, $|H^*+kz-H_0|$.

EXPERIMENTAL PROCEDURE

In the experiments we use a 3-cm-range superheterodyne ENDOR spectrometer at room temperature with a frequency $\nu_{mw}=9400$ MHz. The nonuniform magnetic field is applied along the direction (the z axis) perpendicular to the static magnetic field **H** by placing two wedges on the pole tips of an electromagnetic, as shown in Fig. 1. The change caused in the magnetic field by these wedges in the gap of the magnet is monitored with a Hall pickup. The measurements show that, to within $\pm 0.1\%$, the magnetic field strength varies linearly in z with a gradient $dH(z)/dz=25$ G/mm, while it remains uniform in the perpendicular plane.

As test samples we use LiF single crystals with F-centers. These particular crystals were chosen because the ENDOR frequencies and the dynamics of these crystals have been studied thoroughly.[6–8] All of the test samples are rectangular parallelepipeds with dimensions of $4\times4\times4.7$ mm. The samples are oriented in the magnetic field in such a way that the dimension $l=4.7$ mm runs along the z axis (Fig. 1), while the static magnetic field vector lies in the (001) plane of the crystal (with the cross section of 4×4 mm^2) and makes an angle of 45° with the [100] axis. The experiments show that a reduction of the transverse dimensions of the sample to the sample to 2×2 mm^2 results only in a decrease in the overall intensity of the spectrum, causing no qualitative changes in this spectrum.

We observed the ENDOR of both Li^7 nuclei and F^{19} nuclei in different coordination spheres around the F-center

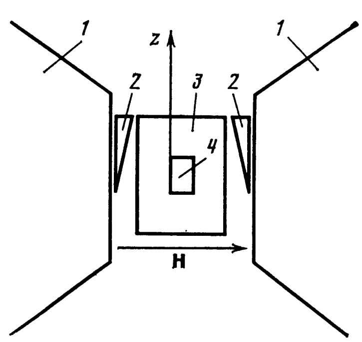

FIG. 1. Schematic diagram of the apparatus used to observe ENDOR in a nonuniform magnetic field. 1—Pole tips of electromagnet; 2—wedge inserts which produce the nonuniform magnetic field along the z direction; 3—microwave resonator; 4—sample; H—static magnetic field.

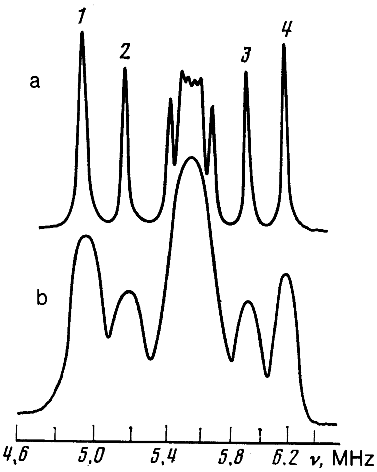

FIG. 2. Spectrum of ENDOR from Li^7 nuclei in (a) a uniform magnetic field (b) a nonuniform magnetic field. Lines 1 and 4, with a width $\delta\nu = 50$ kHz at half-maximum, belong to nuclei of the third coordination sphere. 1—The difference frequency $M = 1/2$); 4—the sum frequency ($M = -1/2$). Lines 2 and 3 ($\delta\nu = 40$ kHz) show the sum and difference frequencies, respectively, of the nuclei of the fifth coordination sphere. The other lines show a superposition of the signals from the nuclei of the third, fifth, and nineth spheres.

in the nonuniform magnetic field. Since we found no fundamental differences in the spectra in the cases of the different nuclei, we devoted most of the effort to the ENDOR signals from Li^7 nuclei near the Larmor frequency of this isotope.

Figure 2 shows the change in the ENDOR spectrum as we switch from a uniform magnetic field to a nonuniform field for a sample with a uniform distribution of paramagnetic centers. This uniform distribution resulted from the particular technique used to produce the paramagnetic centers and was verified by subsequently slicing the sample into thin plates and calibrating measurements of the ESR from each plates. The symmetric broadening of the ENDOR lines in the nonuniform field (Fig. 2b) confirms that there is a uniform distribution of paramagnetic centers. It agrees with expression (3) with $\rho(z) = \text{const}$. Here and below, we are taking the ESR lineshape to be Gaussian, and the ENDOR line shape to be Lorentzian, in the comparison of theory and experiment.

Figure 3 shows ENDOR spectra in a nonuniform magnetic field from samples at whose centers there are diamagnetic "holes" (regions without paramagnetic centers is uniform over the volume of the sample. Both spectra are described well by expression (3) if we set $\rho(z) = \text{const}$ outside the hole and $\rho(z) = 0$ inside it. To illustrate the agreement of theory and experiment, we show in Fig. 3a theoretical values of the ENDOR signal for several characteristic points calculated from expression (3). We see from Fig. 3 that the hole is manifested in the ENDOR spectrum as a doublet splitting of each of the lines. When the size of the hole is increased from 0.5 mm (Fig. 3a) to 1 mm (Fig. 3b), the dip between the components of the doublets becomes significantly deeper, and the distance between the peaks of the doublets increases.

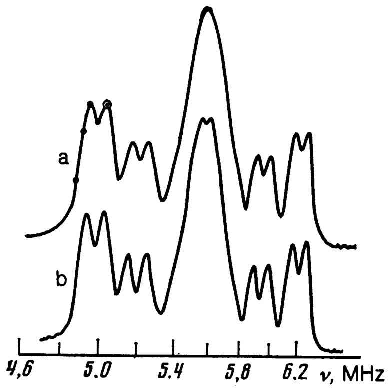

FIG. 3. ENDOR spectrum in a nonuniform magnetic field from samples with a diamagnetic hole, a rectangular parallelepiped with a dimension of 0.5 mm (a) or 1 mm (b) along the z axis. The points are theoretical values of the intensity of ENDOR signal; the point ⊙ is the point at which the theoretical and experimental results are reconciled.

In the ESR spectrum (Fig. 4), the switch from a uniform magnetic field to a nonuniform one results in only an insignificant broadening of the line. The presence of a hole (even of size 1 mm) causes no changes in the spectrum.

During the recording of the ENDOR signals (Figs. 2 and 3), the point of the "landing" along the magnetic field is at the center of the ESR line (in a nonuniform field $H^* = 3296$ G). Figure 5 shows the change in the shape of the ENDOR spectrum in Fig. 3a when the magnetic field is tuned away from the center of the ESR line. These spectra can be described well by the theory [expression (3)] when the corresponding shift of H^* is taken into account.

DISCUSSION OF RESULTS

We begin with a list of the characteristic features of ENDOR in a nonuniform magnetic field: 1) agreement of the shape of the signal, for wide ESR lines and narrow MNR

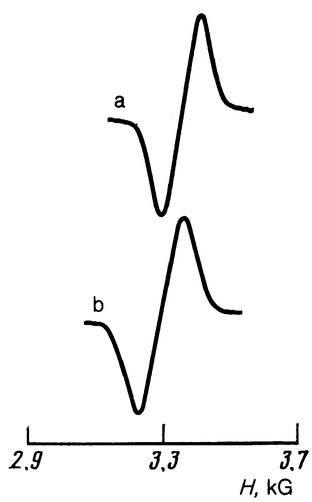

FIG. 4. ESR line (the derivative of the absorption signal) from a sample with a diamagnetic hole 1 mm in size in a uniform magnetic field (a) and a nonuniform field (b). The width of the line (the distance between the extrema of the derivative) in the uniform field is 100 G.

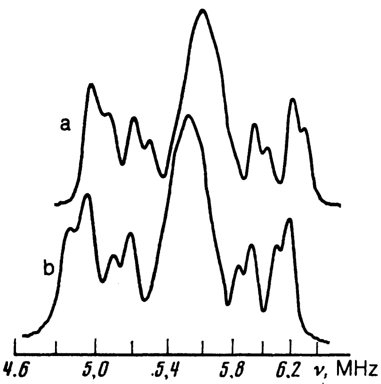

FIG. 5. ENDOR spectrum from a sample with a diamagnetic hole 0.5 mm in size in a nonuniform magnetic field in the case of a "landing" on the wing of the ESR line. a—$H^* = 3268$ G; b—$H^* = 3328$ G.

lines, with the distribution of paramagnetic centers in the sample [see (7)]; 2) spatial focusing of the resonance without the use of any additional technical facilities in the case of narrow ESR lines [expression (9)]; 3) relative intensification of the signal from the part of the sample $\Delta z \sim k^{-1}\delta H$, where the magnetic field is close to the resonant value, and the associated unusual dependence of the shape of the spectrum on the "landing" site on the ESR line [expression (3); Fig. 5] for intermediate values of the widths of the resonance lines.

What are the possibilities in using ENDOR in a nonuniform magnetic field for subsurface imaging? As we have already mentioned, although in ENDOR we are detecting a signal from nuclei, the information on the spatial structure of the object is the same as that from ESR subsurface imaging but fundamentally different from that from NMR subsurface imaging, where the distribution of the nuclei of the matrix of the object is detected. These nuclei are unrelated to any impurities or defects. Consequently, in discussing the applied aspects of ENDOR in a nonuniform magnetic field it is worthwhile to examine the distinctions between the ENDOR method and the corresponding ESR method and the advantages of the ENDOR method.

It follows from the equations derived in the theoretical part of this paper that ENDOR subsurface imaging is most effective in the case of broad ESR lines (100–1000 G). Since the widths of ENDOR lines correspond roughly to the widths of NMR lines in a solid (1–100 kHz), for given values of the gradient of the magnetic field, the spatial resolution in the ENDOR method,

$$\Delta z^{\rm ENDOR} \approx \delta\nu\gamma^{-1}[dH(z)/dz]^{-1},$$

may be several orders of magnitude higher than that in the ESR method,

$$\Delta z^{\rm ESR} \approx \delta H[dH(z)/dz]^{-1}.$$

The improvement in resolution can be estimated from

$$\delta \equiv \Delta z^{\rm ESR}/\Delta z^{\rm ESR} \approx \gamma\delta H/\delta\nu. \qquad (10)$$

With $\gamma = 2$ kHz/G, $\delta H = 100$ G, and $\delta\nu = 1$ kHz, for example, we find $\delta \approx 100$ from expression (10). In our experiments, where the widths of the ENDOR lines are far from the optimum values, we have $\delta \approx 5$, but even this slight improvement made it possible to detect a diamagnetic hole 0.5 mm in size in the sample. This could not have been done by the ESR method alone (Fig. 4). In the case of wide ESR lines ($\delta H > 100$ G), which make ESR essentially worthless for subsurface imaging, ENDOR may be the only method for obtaining information on subsurface paramagnetic centers.

In addition to its high resolution, ENDOR subsurface imaging has the following advantages: 1) The spectrum is recorded in a fixed magnetic field, so that changes in the field gradient during the recording of the signal are eliminated. 2) Since the absorption line itself, rather than its derivative, is recorded, the analysis of the results is simple and clear. 3) There are many ENDOR lines incorporating the same information (the different lines belong, for example, to nuclei of different types or to nuclei of the same type in different coordination spheres), so that it is possible to select an optimum version for subsurface observations, and it is possible to construct a large number of independent equations for the mathematical processing and testing of the results. 4) In the case of narrow ESR lines it is possible to distinguish the ENDOR signal from a small zone of the sample and to obtain from the characteristics of the resonance line (from, say, the magnitude of the quadrupole splitting and the width) precise information on the local properties of the object, unobtainable by other methods.

We believe that ENDOR in a nonuniform magnetic field can be used to greatest advantage in research in solid state physics, particularly on crystals. However, in looking over the list of objects in which this phenomenon might be used we should not ignore amorphous solids and liquids; although ENDOR is observed more rarely in such systems, it does occur.

We note in conclusion that the application of a nonuniform magnetic field reduces the probabilities for transitions due to the dipole-dipole interactions of paramagnetic particles, because of the deviation from the resonant frequencies. This effect should, in long-range[9] and Larmor[10] ENDOR (whole mechanisms include a relaxation of nuclei through paramagnetic centers, a macroscopic diffusion of nuclear polarization, and a cross relaxation), lead to changes in the intensity and nature of the signal, by analogy with the decrease in the concentration of paramagnetic particles. There is the hope that experiments in this direction will make it possible to obtain new information on dynamic processes in crystals near paramagnetic centers.

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