ELECTRON-NUCLEAR DOUBLE RESONANCE OF F CENTERS IN LiF

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The electron-nuclear double resonance (ENDOR) method was used at T = 300 and 20°K to study the magnetic hyperfine interaction of the F centers in LiF with the crystal lattice nuclei in coordination spheres III–IX. The angular dependences of the ENDOR frequencies were investigated in detail at T = 20°K. A general form of the spin Hamiltonian was used to describe the experimental results. The magnetic hyperfine interaction constants were determined. The temperature dependence of the constants was detected and measured in the 20–300°K range.

INTRODUCTION

THE F centers in LiF have been investigated by the ENDOR method before.[1-3] The constants representing the magnetic hyperfine interaction of the F-center electron with the nuclei in three coordination spheres of the crystal lattice, have been determined first by Lord.[1] However, Lord has erroneously taken sphere VIII for sphere II and, therefore, he has drawn incorrect conclusions about the localization of the F-center wave function near a vacancy.

The hyperfine interaction constants for sphere II, determined experimentally in[1] are considerably smaller than the values calculated theoretically in[4]. This disagreement between the theory and experiment has been removed in[2,3] where the EPR and ENDOR of the F centers in LiF have been investigated in detail. The hyperfine interaction constants of sphere II, determined by the ENDOR method, have been found to be much larger than for sphere I. This is in agreement with the theoretical values of these constants and with the EPR experiments, in which the observed hyperfine structure has been found to consist of 35 lines. The ENDOR method has been used to determine the hyperfine interaction constants of an F center in LiF for spheres I–VIII at 1.3°K. However, the use of an axial spin Hamiltonian has given incorrect values of the constants for spheres of lower symmetry.

In the present investigation the steady-state ENDOR method was used to measure the hyperfine interaction constants of an F center in LiF for spheres III–IX at temperatures of 20 and 300°K. In analysis of the experimental data we used the general form of the spin Hamiltonian making allowance for deviations from the axial symmetry. In expressions for the ENDOR frequencies we included the terms associated with a deviation of the nuclear-spin quantization axis from the direction of a magnetic field H_0.[5] Allowance for these terms was essential because of a considerable dipole-dipole hyperfine interaction which—in the case of many spheres—was larger than the contact interaction.

EXPERIMENTAL METHOD AND TECHNIQUE

We used LiF single crystals grown by the Kyropoulos method. Attempts to color crystals additively by means of Na, K, or Cs—as in[6]—were unsuccessful. F centers were produced by bombardment with γ rays from a cobalt gun. The radiation dose was 10^7 rad. units. The optical absorption spectrum of an irradiated LiF crystal is shown in Fig. 1. Line 1 in Fig. 1 represents the F band, and line 2—the M band. The ratio of the line intensities was F/M ≈ 6. The concentration of the F centers, determined from the optical measurements, was 10^{18} cm^{-3}. Identical results were obtained for a neutron-irradiated sample.

The investigation was carried out using an ENDOR superheterodyne spectrometer, operating in the 3-cm range ($\nu_{\text{microwave}}$ = 9290 MHz).[7] The sample was rotated in a (001) plane. The low-temperature measurements were carried out using a cryostat described in[8]. In this cryostat the temperature of a sample was several degrees higher than liquid hydrogen temperature.

EXPERIMENTAL RESULTS AND DISCUSSION

The following expression was used to describe the experimental results for the ENDOR frequencies[5,8]:

$$h\nu = h\nu_L \pm {}^1/_2[a + b_1(3\cos^2\alpha - 1) + b_2(3\cos^2\beta - 1) + {}^9/_8(b_1\varepsilon_1\sin^2 2\alpha + b_2\varepsilon_2\sin^2 2\beta - 8b_1\varepsilon_2\cos^2\alpha\cos^2\beta)], \quad (1)$$

where ν_L is the nuclear Larmor frequency; a is the isotropic hyperfine interaction constant;

$$b_1 = -{}^1/_3(D_{11} + 2D_{22}), \quad b_2 = {}^1/_3(D_{11} - D_{22}), \quad (2)$$

D_{11} and D_{22} are the components of the anisotropic hyperfine interaction tensor; α and β are the angles between the magnetic field H_0 and the principal axes I and II of

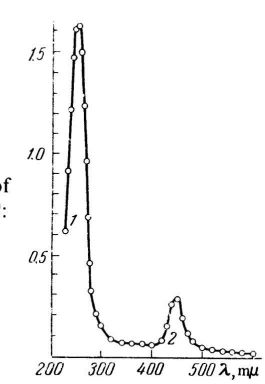

FIG. 1. Optical absorption spectrum of a γ-irradiated LiF crystal [log(I_0/I) = f(λ)]: 1) F band; 2) M band.

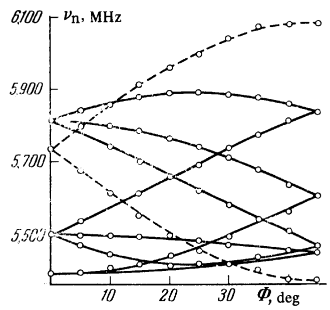

FIG. 2. Angular dependences of the ENDOR sum frequencies for the Li^7 nuclei in spheres III and V; T = 20°K. The dashed curves represent sphere III and the continuous curves—sphere V.

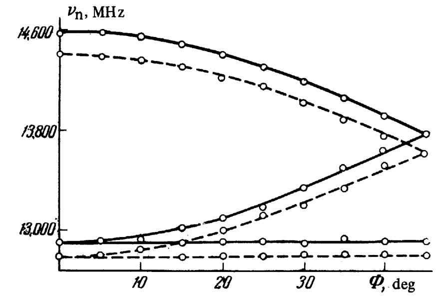

FIG. 4. Angular dependences of the ENDOR frequencies for the F^{19} nuclei in sphere IV. The dashed curves correspond to T = 300°K and the continuous ones—to T = 20°K.

the tensor D_{pq}, respectively; p and q represent the axes of a Cartesian system of coordinates;

$$\varepsilon_1 = \frac{b_1}{\pm 2\nu_L + a + b_1 + b_2}, \qquad \varepsilon_2 = \frac{b_2}{\pm 2\nu_L + a + b_1 + b_2} \tag{3}$$

The signs ± represent, respectively, the sum and difference frequencies.

In the case of an axial spin Hamiltonian, we may assume that $b_2 = 0$, $b_1 = b$ in Eq. (1).

Figure 2 shows the angular dependences of the ENDOR frequencies of the Li^7 nuclei in spheres III and V; ν_L = 5.464 MHz. The dashed curves represent the theoretical dependences for sphere III; the continuous curves represent the theoretical dependences for sphere V; the points are the experimental values. We can see that the agreement between the theory and experiment is good. These angular dependences of the ENDOR frequencies were recorded at T = 20°K.

The curves for coordination spheres IXa and, tentatively, IXb are observed only for some of the angles.

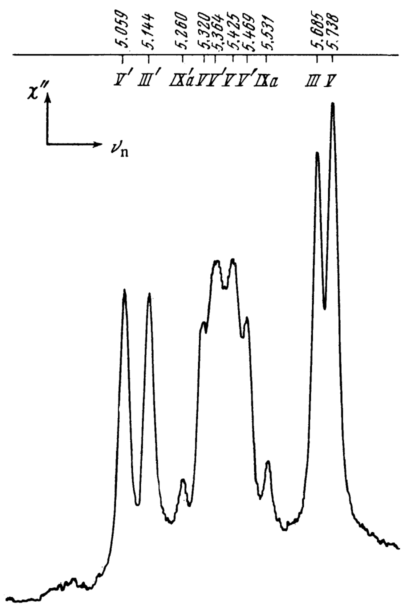

FIG. 3. ENDOR spectrum of the Li^7 nuclei in spheres III, V, IXa; $\Phi = 0°$, T = 300°K, ν_L = 5.396 MHz. The number of the sphere is indicated in the top part of the figure. Primes are used to denote the difference frequencies. χ'' is the imaginary part of the paramagnetic susceptibility and ν_n is the radio-frequency signal.

Sphere IXa has a clearly visible one upper line, which makes it possible to identify this sphere reliably. Sphere IXb has only one line at Φ equal to 25, 35, and 40°; Φ is the angle between the magnetic field H_0 and the [100] crystal axis. These results indicate that the wave function of an F center is most strongly localized along directions of the [110] type. Therefore, it is reasonable to assume that the observed line is due to sphere IXb and not due to spheres XI or XIII, whose nuclei are located further from the vacancy and from directions of the [110] type. The error in the determination of the constants of sphere IXb is much larger than for the constants of other spheres.

The last terms in Eq. (1) are most important in the case of sphere III and are approximately equal to 20 kHz. Since the lines corresponding to the sum and difference frequencies shift in the same direction, their symmetry with respect to the nuclear Larmor frequency is disturbed. This is observed experimentally.

Figure 3 shows the spectrum of the ENDOR lines of the Li^7 nuclei in spheres III, V, and IXa for $\Phi = 0°$ and T = 300°K.

Figure 4 gives the angular dependences of the ENDOR frequencies for the F^{19} nuclei in sphere IV; ν_L = 13.223 MHz. The dashed lines represent the angular dependences at T = 300°K; the continuous lines show the dependences at T = 20°K. The rapid variation of the constant a can be seen clearly in Fig. 4. The change in the constant b is slight.

The angular dependences of the ENDOR frequencies for spheres VI and VIII are shown in Fig. 5. The continuous lines are the theoretical dependences for sphere VI; the dashed curves are the corresponding dependences for sphere VIII. These angular dependences were recorded at T = 20°K.

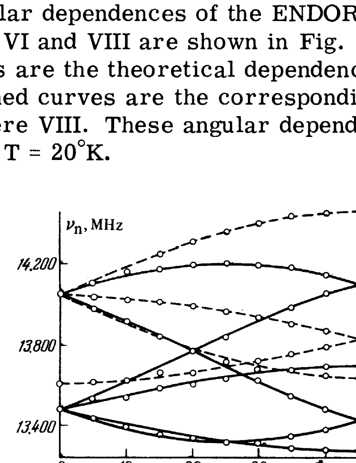

FIG. 5. Angular dependences of the ENDOR frequencies for the F^{19} nuclei in spheres VI and VIII. The continuous curves represent sphere VI and the dashed curves represent sphere VIII; T = 20°K.

Sphere	Type of nucleus	Constant	Published data $T=1.3°$ K [3]	Our measurements $T=20°$ K	Our measurements $T=300°$ K
I	Li^7	a	39,06	—	—
		b	3,20	—	—
II	F^{19}	a	105,94	—	—
		b	14,96	—	—
III	Li^7	a	0,5	0,497	0,550
		b	0,68	0,688	0,676
IV	F^{19}	a	0,48	0,47	0,21
		b	1,12	1,13	1,08
V	Li^7	a	0,27	0,200	0,200
		b_1	0,28	0,333	0,333
		b_2	—	0,016	0,016
		φ**	—	24°20	24°20′

Sphere	Type of nucleus	Constant	Published data $T=1.3°$ K [3]	Our measurements $T=20°$ K	Our measurements $T=300°$ K
VI	F^{19}	a	0,88	0,88	0,88
		b_1	0,69	0,74	0,69
		b_2	—	0,05	0,02
		φ	—	34°45′	34°
VIII	F^{19}	a	1,34	1,34	1,30
		b_1	0,56	0,56	0,55
		b_2	—	0,02	0
IXa	Li^7	a	—	0,072	0,104
		b	—	0,105	0,083
IXb	Li^7	a	—	(0,1)***	—
		b	—	(0,1)	—
N	F^{19}	a	—	(0,1)	—

*a and b are in MHz.

**φ – angle between nearest crystallographic axis and principal axis III of the tensor of anisotropic hyperfine interaction.

***The parentheses indicate inexact results.

A line of a more distinct sphere is observed near the nuclear Larmor frequency of F^{19}. The angular dependence of this line is weak and, therefore, neglecting the anisotropic hyperfine interaction, we can estimate the constant a. This constant is of the order of 100 kHz. In the table this sphere is denoted by N.

Figure 6 shows a typical ENDOR spectrum for the nuclei in spheres IV, VI, VIII, and N; $\Phi = 35°$K, $T = 300°$K.

The table lists the magnetic hyperfine interaction constants of an F center in LiF, obtained at 20 and 300°K. In addition to our results, the table includes also those reported in[3]. At $T = 20°$K our results are in agreement with those reported in that paper. The small difference between the constants for spheres V and VI is due to our allowance for the deviation of the spin Hamiltonian from the axial symmetry. The error in the determination of the constants of the F^{19} nuclei does not exceed 10 kc and in the case of the Li^7 nuclei it does not exceed 5 kc.

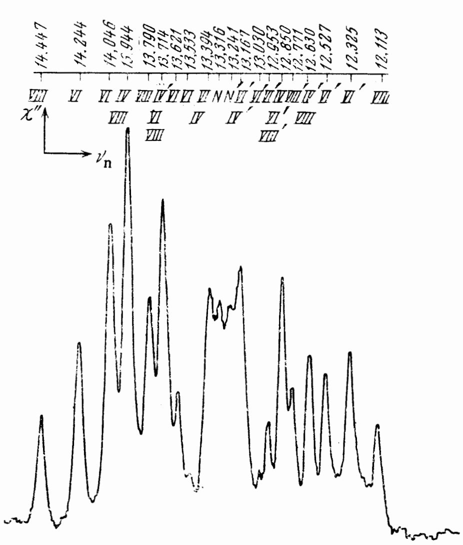

FIG. 6. ENDOR spectrum of the F^{19} nuclei in spheres IV, VI, VIII, and N. $\Phi = 35°$, $T = 300°$ K, $\nu_L = 13.280$ MHz.

When the temperature is increased from 20 to 300°K the constant a of the Li^7 nuclei increases and the constant b decreases slightly. In the case of the F^{19} nuclei, both constants a and b decrease: a changes considerably and b slightly. The greatest change in the constants is observed near room temperature. For this reason the effect has not been observed before.

We must mention that the wave function of an F center is localized mainly along equivalent directions of the [110] type. This is confirmed by an increase in the constants and a stronger intensity of the lines for those spheres in which the nuclei are located closest to directions of the [110] type, even when compared with the nuclei in spheres which lie closer to the vacancy but further from these directions.

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