

all in units of 10^{11} dyne cm^{-2} . From these data, the limiting value of Debye temperature θ for indium was calculated numerically by the method described elsewhere.⁵ The value obtained is

$$\theta = 111.3^\circ\text{K}, \quad (1)$$

with an estimated uncertainty about one percent.

At sufficiently low temperatures, the heat capacity of superconducting indium can be expressed as

$$C_s = \alpha_s T^3 + C_q, \quad (2)$$

where C_q is the nuclear quadrupole heat capacity. Thus a plot of $(C_s - C_q)/T$ versus T^2 should be a straight line through the origin. Such a plot obtained from the calorimetric data¹ is shown in Fig. 1. The straight line through the origin has been drawn to give a slope corresponding to the value of Debye temperature obtained above. A parallel line has been drawn through the normal state points. It can be seen that this latter line gives a good fit to the data below about 0.7°K ; the corresponding value of the coefficient of the electronic heat capacity is $\gamma = 1.65$ millijoule $\text{mole}^{-1} \text{deg}^{-2}$. At low temperatures the calorimetric data in the superconducting state lie considerably below the computed line. The discrepancy is well outside the estimated uncertainty in the slope of the latter. The calorimetric data for $T > 0.7^\circ\text{K}$ doubtless include an electronic contribution. Bryant and Keesom¹ state that below this temperature the electronic term is negligible; even if this were not strictly correct, the discrepancy between the lattice heat capacity computed in the present work and that measured calori-

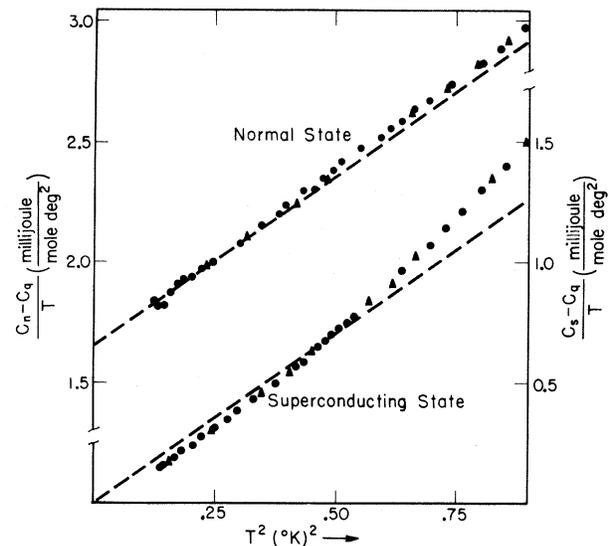


FIG. 1. A plot of $(C_n - C_q)/T$ and $(C_s - C_q)/T$ versus T^2 , from reference 1. The broken straight lines are drawn with a slope corresponding to $\theta = 111.3^\circ\text{K}$.

metrically would only be greater. No reasonable explanation of this discrepancy can be advanced.

¹C. A. Bryant and P. H. Keesom, Phys. Rev. Letters 4, 460 (1960).

²J. A. Rayne, Phys. Rev. 115, 63 (1959).

³W. P. Mason and H. E. Bommel, J. Acoust. Soc. Am. 28, 930 (1956); B. Welber and S. L. Quimby, Acta Met. 6, 351 (1958); D. F. Gibbons and C. A. Renton, Phys. Rev. 114, 1257 (1959).

⁴G. A. Alers and J. R. Neighbours, Revs. Modern Phys. 31, 675 (1959).

⁵J. A. Rayne and B. S. Chandrasekhar, Phys. Rev. 120, 1658 (1960).

RESOLVED HYPERFINE SPECTRA OF ELECTRON-SPIN PARAMAGNETIC RESONANCE IN IRRADIATED LiF^\dagger

Y. W. Kim,* R. Kaplan, and P. J. Bray

Department of Physics, Brown University, Providence, Rhode Island

(Received December 1, 1960)

Recently, Holton, Blum, and Slichter¹ reported on the resolved hyperfine spectra of the electron-spin paramagnetic resonance (ESPR) absorption of F centers in x-irradiated single crystals of LiF . Their spectra are nearly Gaussian in shape with a width (ΔH) of 85 ± 10 gauss from peak to center of the derivative of the ESPR absorption curve. The center of resonance (H_0) of each spectrum corresponds to $g = 2.0006 \pm 0.0006$. The

resolved hyperfine lines, 35 in number, are uniformly spaced, the spacing being approximately 14 gauss when the magnetic field (H) is parallel to a $[100]$ axis or a $[111]$ axis of the sample. No variation of the spacing with orientations of the samples in the magnetic field was reported. Further, Holton et al.¹ measured, by means of electron-nuclear double resonance, the hyperfine coupling constants of the F -center

electron with nuclei up to and including the eighth shell of nuclei surrounding the F^- ion vacancy. The measured values of these constants agree approximately with values predicted by Gourary and Adrian.²

In the present Letter evidence will be presented supporting the view that the hyperfine structure observed in the ESR spectra of irradiated LiF cannot be ascribed simply to the presence of F centers in the crystal. This evidence has been obtained from comprehensive investigations³ of LiF single crystals obtained from the Harshaw Chemical Company and exposed at room temperature to 40-kv x rays, thermal neutrons, or γ rays over a large range of doses. A Varian Model V-4500 spectrometer was employed to obtain the ESR spectra at either 300°K or 77°K. The hyperfine spectra obtained differ from those of Holton *et al.* with respect to shape, width, g value, and angular dependence.

Two distinct shapes of ESR spectra were observed. One was Gaussian, and the other Lorentzian. The spectra of Gaussian shape were obtained from samples which were irradiated with x rays, γ rays, and neutrons, with doses up to 10^{18} nvt. These spectra gave values of $\Delta H = 60 \pm 6$ gauss and $g = 2.0027 \pm 0.0004$, regardless of the radiation dose. The concentration of electron spins responsible for the Gaussian resonance was found to be of the order of $10^{17}/\text{cm}^3$ for neutron doses of approximately 10^{14} nvt. It increased almost linearly for neutron doses up to about 10^{16} nvt, after which it asymptotically approached a constant value of the order of $10^{20}/\text{cm}^3$. In these samples it was found that the concentration of F centers estimated by means of optical absorption agreed, in order of magnitude, with the concentration of electron spins found for various neutron doses. By means of power saturation, this Gaussian resonance was found to be inhomogeneously broadened. Spectra of Lorentzian shape were obtained from some samples with neutron doses of approximately 10^{16} nvt or more. H_0 of these spectra corresponds to $g = 2.0023 \pm 0.0004$. The observed ΔH varied from sample to sample, with a maximum value of 35 ± 4 gauss, and appeared to decrease as neutron doses increased. In an earlier paper, the authors have associated the Lorentzian resonances with conduction electrons in Li metal grains formed in LiF.⁴

The anisotropy of the ESR spectrum was investigated by rotating the sample about its [110] axis, which was held perpendicular to the direc-

tion of the magnetic field. In this case, the magnetic field sweeps over the (110) plane of the sample. The angle between the [001] axis and H direction is denoted by α .

All spectra, whether Gaussian or Lorentzian in shape, clearly exhibited partially resolved hyperfine lines of uniform spacing at $\alpha = 0^\circ, 55^\circ, 72^\circ,$ and 90° , while they were unresolved and "smooth" at $\alpha = 25^\circ$ and 80° . For both shapes of spectra, the spacing of lines at $\alpha = 0^\circ, 55^\circ, 72^\circ,$ and 90° is approximately 14 gauss, 14 gauss, 7 gauss, and 12.5 gauss, respectively. The change of a resolved spectrum (or a smooth spectrum) into a smooth spectrum (or a resolved spectrum) as α increases from 0° to 90° takes place gradually. Figure 1 exhibits a resolved hyperfine spectrum of Gaussian shape with $\Delta H = 60 \pm 6$ gauss, which was observed near $\alpha = 72^\circ$. The uniform spacing between lines is 7 gauss. Figure 2 shows a resolved hyperfine spectrum of Lorentzian shape with $\Delta H = 35 \pm 4$ gauss which was observed at $\alpha = 55^\circ$. The resolved hyperfine lines are spaced 14 gauss apart. Table I lists the anisotropy of line spacing, and the number of resolved hyperfine lines. It should be noted that, in spite of the anisotropy of line spacing, the envelopes of the resolved spectra of both shapes exhibited no noticeable dependence on α .

Some resonance curves of Gaussian shape were transformed into Lorentzian or other shapes by heat-treating the sample. A sample with 4.2×10^{16} nvt irradiation, and a sample with 5×10^{16} nvt irradiation, both of which yielded the Gaussian

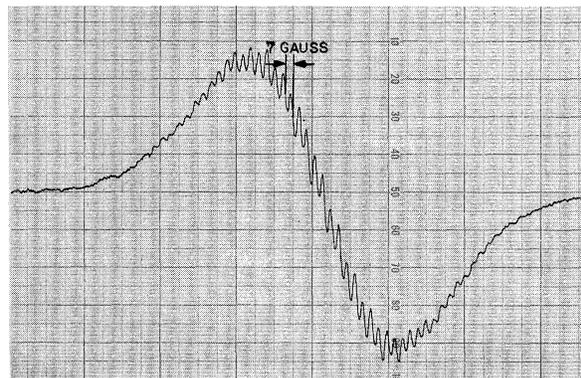


FIG. 1. Resolved hyperfine spectrum of Gaussian shape representing an ESR absorption in an irradiated single crystal of LiF (neutron dose: 1.3×10^{15} nvt), when the angle of rotation, α , is near 72° . The center of resonance H_0 corresponds to $g = 2.0027 \pm 0.0004$, and the spacing between neighboring hyperfine lines is approximately 7 gauss.

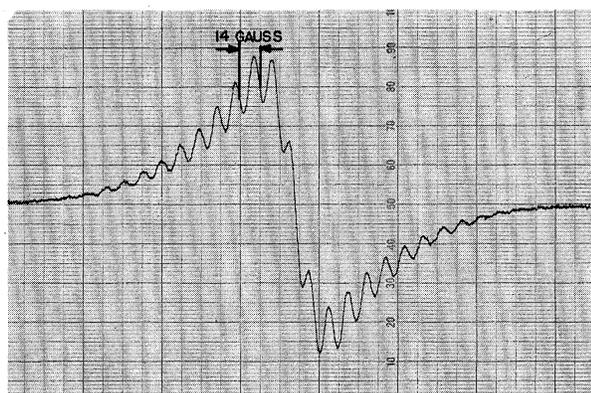


FIG. 2. Resolved hyperfine spectrum of Lorentzian shape representing an ESR absorption in an irradiated single crystal of LiF (neutron dose: 9.9×10^{17} nvt), when the angle of rotation, α , is 55° . The center of resonance corresponds to $g = 2.0023 \pm 0.0004$, and the spacing between neighboring hyperfine lines is 14 gauss.

shape of ESR spectrum, were heat treated for two hours at 250°C , followed by a rapid quenching to room temperature, and for one and one-half hours at 200°C , followed by a slow anneal to room temperature, respectively. After these thermal treatments, the former sample yielded a spectrum of Lorentzian shape, with $\Delta H = 27$ gauss, while the spectrum of the latter had neither a Gaussian nor a Lorentzian shape. The anisotropy of the resolved hyperfine structure of these spectra remained unchanged.

The experimental results presented here suggest the following possible mechanisms: the resolved hyperfine spectrum of Gaussian shape is caused by two distinct types of paramagnetic centers. Centers of Type I are not affected by thermal treatment, and are responsible for the anisotropic hyperfine structure, which remains unchanged after heating. Centers of Type II are more easily affected by thermal treatments, and are responsible for that part of the resonance that changes in shape from Gaussian to Lorentzian (or from Gaussian to other forms) upon heating. The data suggest that the major part of the Gaussian resonance is caused by centers of Type II.

Table I. Angular dependence of resolved hyperfine structure appearing with ESR spectra of both Gaussian and Lorentzian shapes which are obtained from irradiated single crystals of LiF.

α	Spacing	Minimum number of resolved lines
0°	14 gauss	19
25°	...	No resolved lines
55°	14 gauss	37
72°	7 gauss	45
80°	...	No resolved lines
90°	12.5 gauss	17

Since the spin concentrations responsible for the Gaussian resonances of irradiated samples agreed, in order of magnitude, with the F -center concentrations in these samples, the Type II center is probably an F center. The Type I center may consist of some impurity paramagnetic ion occupying possibly the F^- ion vacancy or perhaps the Li^+ ion vacancy.

Agreement between our resolved hyperfine spectra of Gaussian shape and the spectra of Holton *et al.* is seen in the 14-gauss spacing of hyperfine lines at $\alpha = 0^\circ$ ($H \parallel [001]$ axis) and at $\alpha = 55^\circ$ ($H \parallel [111]$ axis).

Further investigations appear to be necessary to make all the results compatible.

†This research was sponsored by the U. S. Atomic Energy Commission.

*Present address: Department of Physics, Wayne State University, Detroit, Michigan.

¹W. C. Holton, H. Blum, and C. P. Slichter, *Phys. Rev. Letters* **5**, 197 (1960).

²B. S. Gourary and F. J. Adrian, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1960), Vol. 10, p. 128.

³Y. W. Kim, R. Kaplan, and P. J. Bray, *Bull. Am. Phys. Soc.* **3**, 178 (1958); **4**, 261 (1959); and **5**, 252 (1960).

⁴Y. W. Kim, R. Kaplan, and P. J. Bray, *Phys. Rev.* **117**, 740 (1960).

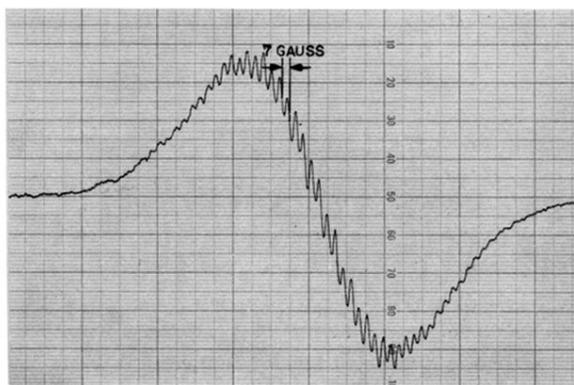


FIG. 1. Resolved hyperfine spectrum of Gaussian shape representing an ESR absorption in an irradiated single crystal of LiF (neutron dose: 1.3×10^{15} *nt*), when the angle of rotation, α , is near 72° . The center of resonance H_0 corresponds to $g = 2.0027 \pm 0.0004$, and the spacing between neighboring hyperfine lines is approximately 7 gauss.

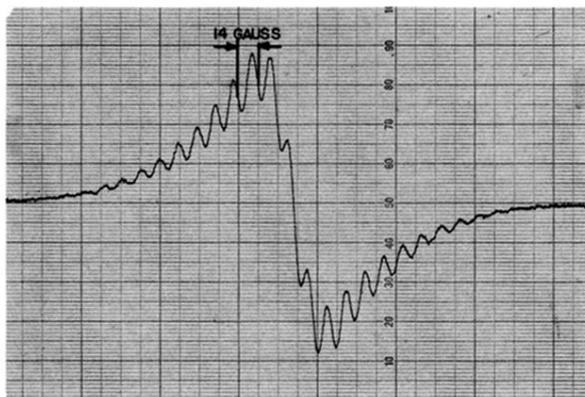


FIG. 2. Resolved hyperfine spectrum of Lorentzian shape representing an ESR absorption in an irradiated single crystal of LiF (neutron dose: 9.9×10^{17} nvt), when the angle of rotation, α , is 55° . The center of resonance corresponds to $g = 2.0023 \pm 0.0004$, and the spacing between neighboring hyperfine lines is 14 gauss.