the observation.

It is interesting to note that the absorption lines of impurities are very much sharper in germanium than in silicon. The full width at half absorption is about 0.19×10^{-3} ev for the observed lines of Cu and the group III impurities. The actual width is probably even smaller, since the observed width is comparable to the resolution used. This is to be compared with the width of 1×10^{-3} ev reported for boron lines in silicon.[7] The broadening of the absorption lines has been treated[7,8] theoretically on the basis of the scattering of the bound hole by the acoustical vibration of the lattice. According to these treatments which used the hydrogenic approximation for the impurity, the width is determined mainly by the broadening of the ground state, and for germanium and silicon the ratio of the widths is expected to be of the order of the reciprocal of the Bohr radius squared. On this basis, we would expect the lines of the group III impurities to be 6 to 7 times narrower in germanium than in silicon. The observation shows that the ratio of the linewidths in these two materials is at least as large as this estimate. The lines of Zn^- are considerably broader, about 0.43×10^{-3} ev in width for the D line. The width is considerably larger than the instrumental resolution. This result further substantiates the expectation that the broadening of the ground state increases with decreasing orbit dimension. In this connection, the failure to observe the excitation lines of Cu^- might be caused by large broadening. The orbit of the hole in the ground state may be quite small for Cu as indicated by the large ionization energy of 0.33 ev.

One additional point of interest is the difference in the relative strengths of the various lines for different impurities. This is particularly pronounced in comparing the spectrum of Zn with that of the group III impurities. The C line is much weaker than the D line in the case of Zn^-. Noticeable variations can be seen even among Cu, Zn, and the group III impurities, which should reflect mainly the difference in the ground states. Accurate data have yet to be obtained.

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HYPERFINE STRUCTURE OF THE F CENTER IN LiF*

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The F center in LiF is one of the color centers in alkali halides which has been most throughly studied experimentally by magnetic resonance[1-8] and theoretically.[9] To date there is serious disagreement between experiment and theory. Lord[2] originally reported resolved structure of the electron spin resonance, which he interpeted as arising from the hyperfine coupling of the electron to the six Li^7 atoms nearest to the vacancy. Although he failed to see all of the 19 lines predicted by this model, he later supported his contention[3] with the direct measurement of the hyperfine constants by the electron-nuclear double resonance technique (ENDOR).[10] Stimulated by this work, Gourary and Adrian[9] calculated the hyperfine coupling with the nearby nuclei. While the agreement with the nearest lithium atoms was satisfactory, the prediction for the nearest fluorine atoms was too large by a factor of 30. The picture was further complicated when Kim, Kaplan, and Bray[4] reported that they could resolve at least 10 more lines than the 19 predicted. Hyde[8]

has even suggested that the resolved structure is not due to the F center.

We have investigated the paramagnetic resonance of x-rayed LiF crystals containing F and M centers. This Letter reports the observation of 35 lines in electron spin resonance (ESR), together with new electron-nuclear double resonance data which enable us to predict the observed electron spin resonance in great detail and to resolve the discrepancy between theory and experiment.

The samples were obtained from Harshaw, and either used without treatment, or annealed in an inert atmosphere, or left exposed to the atmosphere for over a year. They were then exposed to 50-kv x rays at room temperature for varying lengths of time ranging from 1/2 hour to 15 hours. Optical density (OD) measurements show that the F-center concentration is varied from $10^{17}/\text{cm}^3$ to greater than $10^{18}/\text{cm}^3$ while the ratio OD_F/OD_M is varied from 600 to ~3.5. The electron spin resonance is observed both at room temperature and at 1.3°K. The crystal is located midway on the narrow side wall of a TE 101 mode microwave cavity which is slit vertically on the center line of the broad face, the two halves electrically insulated to allow rf penetration from the rf coil wound on the exterior of the cavity for ENDOR experiments at 1.3°K. The X-band paramagnetic resonance spectrometer consists of a transmitter klystron employing a modified Pound i.f. frequency stabilization scheme and a high-sensitivity superheterodyne receiver.

With H_0 parallel to the [100] direction, the electron spin resonances of all specimens exhibit 35 lines with a spacing of ~14 gauss, uniformly decreasing in amplitude from the center of the line and symmetric about $g = 2.0006 \pm 0.0006$. A typical slow-passage derivative record is shown in Fig. 1. To determine whether or not two resonances are present, one broad and structureless, the other possessing structure, we have checked the ratio of the resolved structure amplitude to the broad resonance amplitude of each sample. It is constant to within a factor of 2, thus essentially independent of the F/M concentration ratio for the range of concentrations we have used. The resolution is improved tenfold when H_0 is parallel to [111] and decreased twofold when H_0 is parallel to [110]. The over-all shape of the integrated experimental curve is nearly Gaussian with a width of 85 ± 10 gauss from peak to center of the derivative.

An attempt to explain the excessive number of lines by considering either forbidden transitions or an isotope effect is not successful when one uses Lord's values of the hyperfine couplings.

Electron-nuclear double resonance signals can be grouped, each group arising from a shell of nuclear sites which are crystallographically equivalent with respect to the F-center negative ion vacancy and whose distance from the vacancy is $\sqrt{N}$ times the lattice parameter, where N is an integer. For a given shell N, there are two sets of ENDOR lines arising from cases where the field of the electron at the nucleus either aids

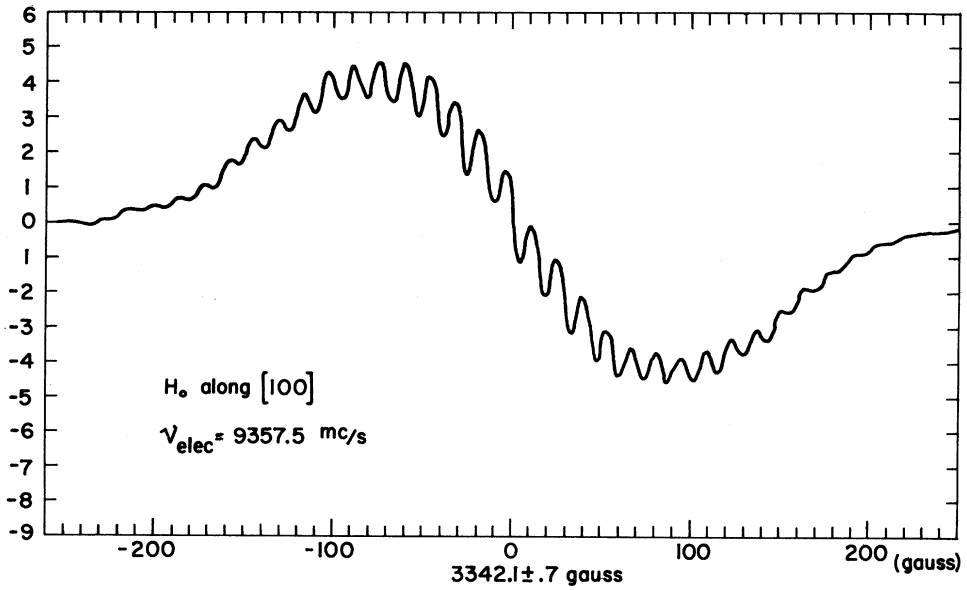

FIG. 1. ESR absorption derivative curve showing 35 resolved lines. H_{mod} = 2 gauss at 800 cps. T = 1.3°K. $H_{\text{microwave}} \sim 3 \times 10^{-5}$ gauss.

or opposes the external field. (We call the two cases respectively "up" and "down.") To check that lines were properly identified as "up" or "down," we have studied the variation of their frequency with external field. We verified that the Shell 1 lines were correctly identified. A search for high-frequency ENDOR lines not previously reported, however, reveals a complete set of lines having the symmetry of Shell 2, the nearest fluorines. The nuclei giving rise to these lines are identified as fluorines from the dependence of the ENDOR frequency on H_0 and by the separation of the "ups" and "downs" by twice the Larmor frequency in the static field (see Fig. 2). From the magnitude of the hyperfine splitting we conclude these are in fact Shell 2 and that Lord's Shell 2 lines are Shell 8. The ENDOR pattern is usually computed using first-order perturbation theory. If the hyperfine coupling is treated to second order, subsidiary splittings arise.[11] Such a set is illustrated by the 4 lines near 31 Mc/sec which arise from the Shell 2 fluorines. The calculation predicts a separation of 0.5 Mc/sec with the intensity ratios 1:4:4:1 as observed. In addition, the ENDOR lines were observed to obey the correct angular dependence of Shell 2 when the crystal is rotated about a [110] axis as well as a [100] axis perpendicular to H_0.

ENDOR lines are identified through Shell 8 (there is no Shell 7 by this scheme of numbering shells); the hyperfine constants a and b are given in Table I together with the theoretically predicted values of Gourary and Adrian. The Shell 1 and Shell 2 values are in rough agreement with the predicted values.

Table I. Hyperfine constants in megacycles/sec for the first seven shells of nuclei surrounding the F center in LiF.

Shell	Nucleus	a	b
1	Li^7	39.06 ± 0.02 (theo. = 50)	3.20 ± 0.01 (theo. = 2.8)
2	F^{19}	104.94 ± 0.02 (theo. = 61)	14.96 ± 0.02
3	Li^7	0.50 ± 0.01	0.68 ± 0.02
4	F^{19}	0.48 ± 0.01	1.12 ± 0.01
5	Li^7	0.27 ± 0.01	0.28 ± 0.01
6	F^{19}	0.88 ± 0.01	0.69 ± 0.01
8	F^{19}	1.34 ± 0.01	0.56 ± 0.01

Using the measured Shell 1 and Shell 2 hyperfine values and assuming a rectangular broadening function to take account of the other shells, we have calculated the detailed ESR line shape for H_0 parallel to [111]. The result is shown in Fig. 3 together with an integrated experimental record and a Gaussian. The calculation predicts an average resolved structure separation 6% greater than the Shell 1 a value. This effect is clearly seen in the integrated experimental ESR curve. Both the experimental and calculated curve are nearly Gaussian. The root second moment, calculated from the measured hyperfine constants, is 75.7 gauss; the measured root second moment (from derivative peaks assuming

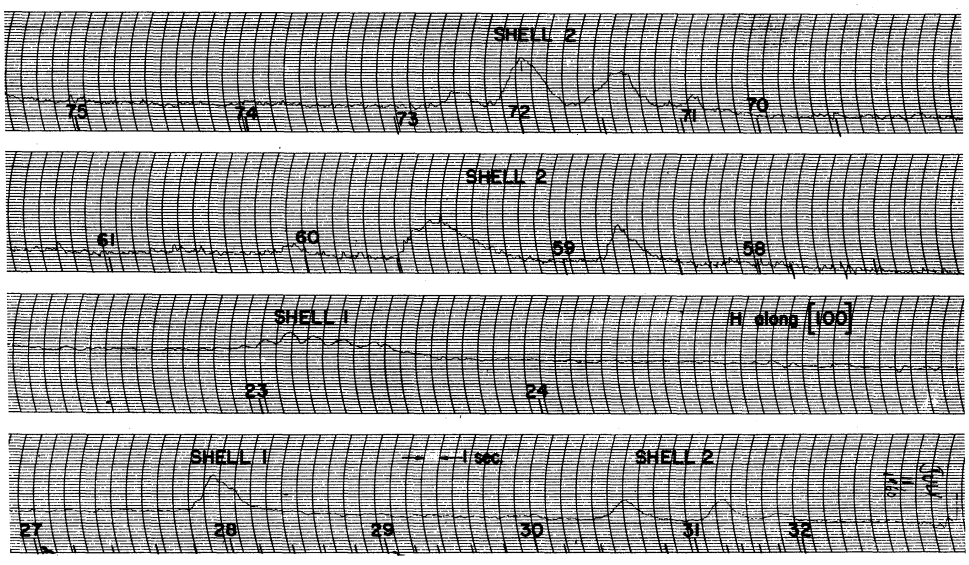

FIG. 2. ENDOR lines showing portions of Shells 1 and 2.

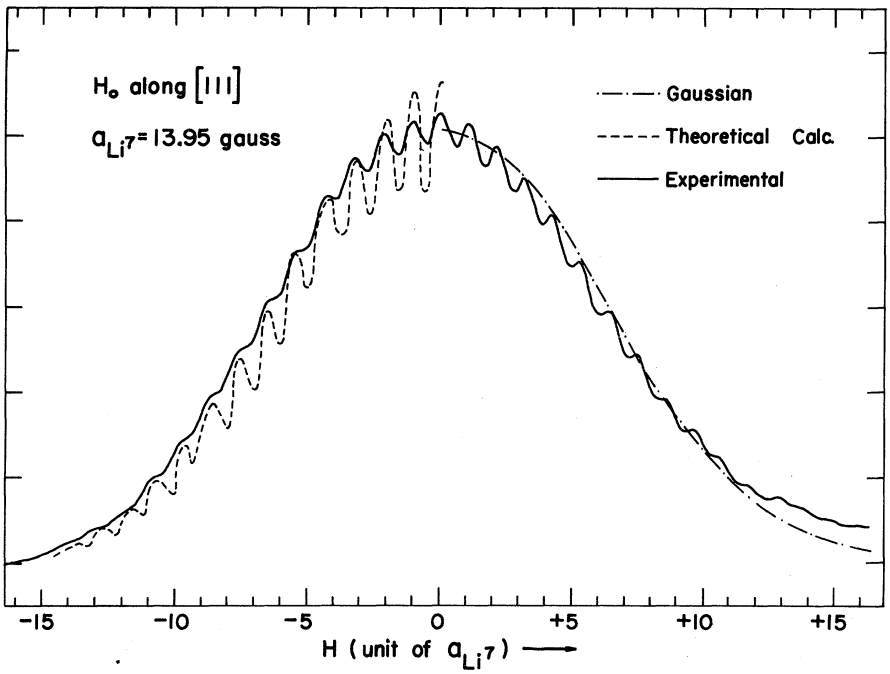

FIG. 3. Comparison of the integral of an experimental ESR curve for H_0 parallel to [111] with the calculated ESR line shape and with a Gaussian curve.

a Gaussian) is 85± 10 gauss. We conclude that substantially the entire resonance arises from F centers, that the observed ENDOR lines account completely for the experimental line shape and are in substantial agreement with the calculations of Gourary and Adrian.

Our new increased second moment for the F center is larger than that attributed by Lord both to the F center alone and to the combination of the F and M centers.[12] If we are correct, Lord's detection of the existence of the M-center resonance by second moment methods is inconclusive.

We would like to thank Professor Robert Maurer for making available his Cary spectrophotometer for determination of the optical spectra, and Dr. J. Kingsley for his helpful advice in its use. A substantial amount of the numerical analysis of the double-resonance data was performed by Mr. Nils Fernelius. The numerical computation of the theoretical line shape was performed by Mr. James Bushnell. We wish to thank Dr. George S. Newell who built the microwave spectrometer in conjunction with two of the authors (WCH and HB).

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