$(glycine)_3 \cdot H_2SeO_4$[7] and $(glycine)_3 \cdot H_2BeF_4$,[8] however; and nothing is known as yet about the switching time of LHzS. The ferroelectric loops are not as square as those of $(glycine)_3 \cdot H_2SO_4$ and isomorphs of the latter.

SPECIFIC-HEAT MEASUREMENTS

Specific-heat measurements were carried out in an adiabatic calorimeter, in the region from −120°C to 205°C. No anomaly was detected in this temperature range.

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V-Type Center Resonance of Neutron-Irradiated LiF at Room Temperature*

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A *V*-type center similar to one described by Känzig and co-workers has been found in LiF single crystals neutron-irradiated at room temperature. Analysis of the *s* and *p* admixture in the electron wave function, using the Hamiltonian of Woodruff and Känzig, is made from the angular dependence of the electron-spin resonance spectrum.

ELECTRON-SPIN paramagnetic resonance (ESPR) investigations at room temperature of neutron-irradiated LiF single crystals have yielded two different groups of hyperfine lines.

The rectangular samples, approximately 0.14 in. ×0.14 in.×0.75 in., were cleaved from large crystals obtained from the Harshaw Chemical Company. Neutron irradiation for periods ranging from 10 minutes to 72 hours was secured at room temperature with a flux of approximately 2.3×10^{12} $n/\text{cm}^2\text{sec}$. After irradiation, the samples were kept at dry-ice temperature until the ESPR experiments were performed with a Varian Associates Model No. 4500 ESPR spectrometer.

The samples were rotated about a [100]-type axis in a dc magnetic field (H_0) perpendicular to the axis of rotation. Two distinct hyperfine groups were observed. One group,[1] in the vicinity of $H_0\simeq 3400$ gauss with a microwave frequency of 9500 Mc/sec, is very intense; the other is much less intense and is spread widely on both sides of the first (Fig. 1). The spacings of the resonances in both groups are dependent on the direction of H_0 and are conveniently analyzed in terms of the angle α between H_0 and either of the [100]-type axes perpendicular to the axis of rotation.

The observed resonance magnetic field for each of the weaker and widely spaced group of lines is indicated by a square in Fig. 2. Solid lines show the shift of each resonance as α ranges from 0° to 45°. The pattern is symmetric about $\alpha=45°$. The lines are distributed over a range of 2000 gauss with the outermost line on each side of the pattern being appreciably weaker than the others. Peak-to-peak widths of these lines are of the order of 50 gauss.

The pattern of the solid lines in Fig. 2 is strikingly similar to the R_1 and R_4 curves of Fig. 10 in the paper of Woodruff and Känzig.[2] A regraphing of the R_1 and R_4 curves of their θ *vs* H diagram into our α *vs* H_0 diagram yields the circles and dotted lines of Fig. 2. The R_2 and R_3 families are obscure in our spectrum because of the strong central resonance. A comparison of the two patterns of Fig. 2 suggests the interpretation that the observed weak and widely spaced lines arise from a *V*-type (F_2^- ion) center similar to the one proposed by Känzig and co-workers.[2,3]

The separation of the lines R_1 and R_4 for $\alpha=45°$ ($\theta=0°$) in our spectrum enabled us to determine $a+b=951$ gauss by means of the approximation formula Eq. (6) of Castner and Känzig[3] which gives $a+b=887$ gauss for $\theta=0°$ in their spectrum. Although a correct estimation of $|a|$ is very difficult in our case, it is estimated to be of the order of 100 gauss by fitting at various θ values. Such analysis indicates that the characteristic shift of our curve relative to Känzig's,

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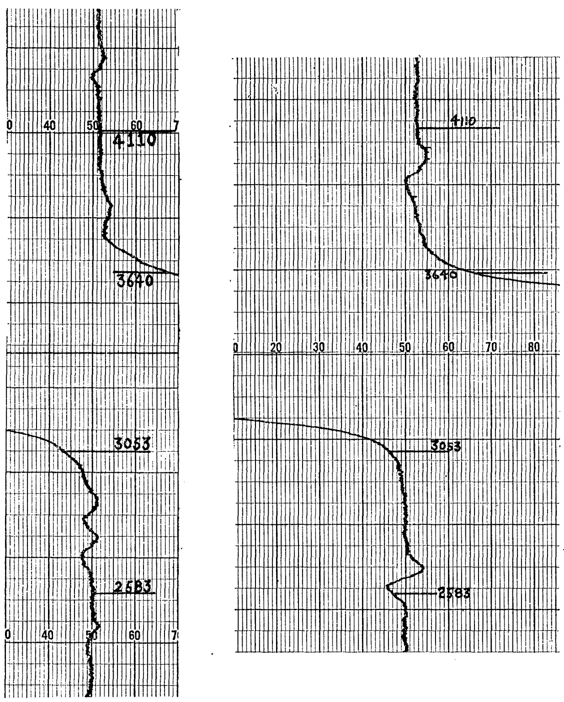
particularly at the higher magnetic fields, is chiefly due to these different values of a and b in the spin Hamiltonian.[3] Using $a+b=951$ gauss and the theoretical expression[3] for $a+b$, the fraction of p-state admixture of the ground state is estimated to be 0.62. This indicates a 30% increase of p-state admixture when compared with the value of 0.49 found by Castner and Känzig.[3]

The large half-width (approximately 50 gauss) of each line is qualitatively attributed to the thermal broadening effect. It is not possible that the H center of Känzig and Woodruff[4] is also contributing to the width. The H center yields a paramagnetic resonance



(a) (b)

FIG. 1. Hyperfine spectrum of neutron-irradiated LiF. The absorption between 3053 gauss and 3640 gauss is the central intense group. The much weaker lines on both sides of the intense group are the hyperfine splittings due to V-type centers. (a) $\alpha=35°$; (b) $\alpha=0°$.

spectrum similar to that of the V center except that each line of the latter is split further. Such further splitting should be observable even under the present experimental conditions.

The observability of a V-type center at room tem-

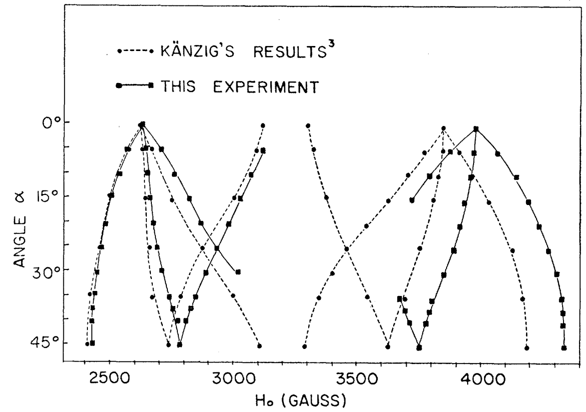


FIG. 2. The resonance magnetic fields for which the R_1 and R_4 lines in the spectrum of the V-type center of neutron-irradiated LiF are observed with a microwave frequency of 9.5 kMc/sec. The fields are plotted as a function of the angle α between one of the [100]-type axes and the direction of the dc magnetic field H_0.

perature in the present experiments may arise from the nature of the regions of severe damage caused by the ${}_3Li^6+{}_0n^1 \rightarrow {}_1H^3+{}_2He^4+4.8$ Mev reaction. The weak intensity of the resonances indicates that relatively few of the V-type centers are in environments which render them stable at 300°K.

Further investigations of the V-center type resonances will attempt to determine whether the observed centers are characteristic only of LiF or perhaps lithium halides—or are present in other alkali halides which have received intensive neutron irradiations at room temperature. Subsequent work will be complemented by low-temperature studies which will permit much higher resolution.

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Noted added in proof.—We are greatly indebted to Dr. Werner Känzig of the General Electric Research Laboratory for communicating to us some recent results of his work on x-ray irradiated LiF. He has found a V center which is an F_2^- molecule-ion associated with a positive ion vacancy (or possibly a vacancy pair). The effect of the association manifests itself essentially in the center group (R_2 and R_3 components) only. It is just this group that we cannot observe. This center is thermally much more stable than the unassociated V center. A similar center is perhaps responsible for the resonances reported in this article.

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