small increases take place at especially half the energy gap and also at other integer fractions of the gap.[2,11] As can be seen from these curves in Figs. 2 and 3, when the samples have been exposed to light, the so-called "mid-gap bump" becomes clearly visible. The thickness of the evaporated CdS film is probably uneven; and, at least at first sight, the experimental results tend to support the explanation given by Schrieffer and Wilkins of multi-particle tunneling.[12]

In summary, these experiments demonstrate that it is possible to tunnel through a properly prepared artificial barrier and that both ordinary tunneling and supercurrent tunneling can be made photosensitive.

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ESR OF A [111] DEFECT IN X-RAYED LiF†

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A new defect center that is believed to be the equivalent of the interstitial halide atom is observed in x-rayed pure LiF. It has the form of a negatively charged diatomic halide molecule situated on a single halide site and orientated along a [111] axis. The ESR constants are $g_x = g_y = 2.0105$, $g_z = 2.0017$, $T_x = T_y = 19.0$ G, and $T_z = 1005.9$ G.

This Letter reports the results of measurements and analysis of an ESR spectrum of a new defect that is produced by x irradiation of LiF at low temperatures. This new defect has [111] symmetry and appears to be the interstitial fluorine defect for pure LiF.

Interstitials are important in several phenomena of solid-state physics. There are many examples of interstitial impurities and interstitials associated with impurities, but interstitials in pure materials have been very elusive. Until recently, it was generally believed that the interstitial halide atom in pure alkali halides was a defect with [110] symmetry. This [110] defect has the form of a negatively charged diatomic halide molecule (e.g., F_2^-) centered on a lattice site and is the result of the combination of an interstitial halide atom with a halide lattice ion. The [110] defect in LiF, KCl, and KBr was studied by Känzig and Woodruff[1] by ESR, and was called the *H* center since it appeared to correspond[2] to the optical *H* band which was first studied by Duerig and Markham[3] after x irradiation of KCl and KBr at liquid-helium temperature. However, a recent electron-nuclear double-resonance (ENDOR) study by Dakss and Mieher[4] has shown that in LiF the [110] defect is associated with a sodium impurity which is located on a nearest-neighbor lithium site. We believe that the new [111] ESR defect[5] is also an F_2^- molecule that is centered on one negative-ion lattice site with the molecular axis in a [111] direction.

The observed angular dependence of the ESR of the [111] defect is shown in Fig. 1 for a rotation of the magnetic field in a $(1\bar{1}0)$ plane. For comparison the angular dependence of the ESR of the self-trapped hole (V_K center), which has [110] symmetry, is also shown. It is well established that the V_K center in the alkali halides has the form of a negatively charged diatomic halide molecule (e.g., F_2^-) located on two lattice sites and is the equivalent of a hole shared by two negative ions in a [110] direction.[6,7] The ESR spectra of all F_2^- (and the other halides) defects are characterized by a large anisotropic hyperfine interaction between the unpaired electron and the two

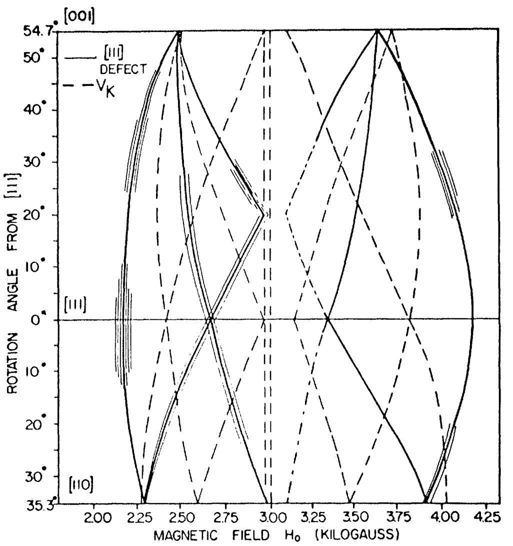

FIG. 1. The angular dependence of the ESR of the [111] defect in LiF for a rotation of the magnetic field in a (110) plane. The narrow lines indicate the "secondary splitting" and the dot-dashed lines indicate the region where the resonance lines lie under the F center resonance.

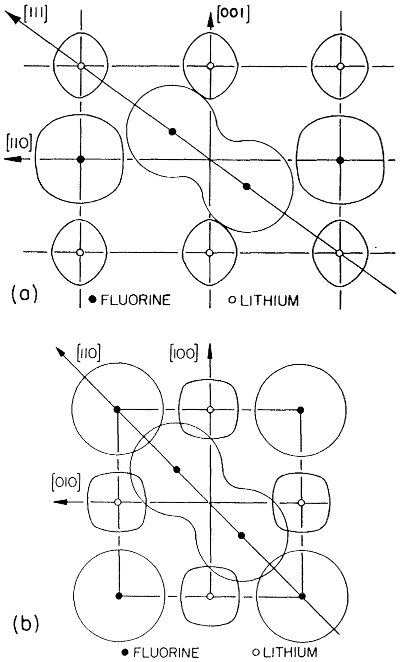

FIG. 2. The F_2^- molecule in LiF for the molecular axis along (a) [111] direction and (b) [110] direction.

nuclei of the molecule. The main difference between the two spectra in Fig. 1 is due to the different symmetries of the defects since both defects are basically F_2^- molecules.

Very few optical studies of x-rayed LiF have been made. In LiF an optical band which corresponds to either the [111] or [110] interstitial defect has not been found. Speculation arises as to whether or not a similar [111] defect exists in other alkali halides. None of the optical bands in KCl and KBr which are thought to involve the interstitial halogen possess [111] symmetry (e.g., V_1,[8] V_4,[9] and H'[10]). Although impurity-associated defects with [111] symmetry have been reported previously,[11,12] we believe that this is the first time that an intrinsic defect with [111] symmetry has been observed in the alkali halides.

It is perhaps not too surprising that the [111] orientation is preferred over the [110] orientation for the pure interstitial defect. Calculations for KCl and NaCl by Dienes, Hatcher, and Smoluchowski[13] have shown that if only electrostatic and ion-core repulsive energy terms are considered, then the [111] orientation has a lower energy than the [110] orientation. Figure 2 contrasts the [111] and [110] orientations for an assumed internuclear distance of 3.8 a.u. for the F_2^- molecule. The lattice ions are shown at their perfect lattice positions, and all contours correspond to 0.3 electrons/Å^3.[14] The distance of 3.8 a.u. gave the best fit for calculations of the V_K-center ENDOR hyperfine constants[15] and this distance is near the theoretical free-F_2^- internuclear distance of 3.6 a.u.[16] Although the lattice can have considerable distortion and the internuclear distance may be less than 3.8 a.u., it certainly appears that there is less crowding for the [111] defect.

We have produced the [111] defect by x rays in high-purity Harshaw LiF at liquid-helium temperature. The production rate is slow. About 30 h of x irradiation[17] is required before the ESR signals are observed with our spectrometer. The growth of the [111] defect is approximately linear up to 300 h (our longest irradiation to date). V_K and F centers are also present. While the V_K center production appears to saturate after ≈100 h, the F center continues to grow. The [111] defect was also produced at temperature up to ≈40°K and is stable up to ≈60°K (compared with ≈105°K for the [110] interstitial defect). ESR has been observed from liquid-helium temperature to about 50°K. Throughout this study, the [110] defect was not observed. Dakss and Mieher[4] produced the [110] defect by x-raying reagent-grade LiF at liquid-nitrogen temperature. Also, they observed no [110] defects after 100-h irradiation of pure Harshaw LiF at liquid-nitrogen temperature.

Table I. Principal values of the g tensor and hyperfine tensor T of the [111] defect, H, and V_K centers in LiF and the V_K and V_{KA} centers in NaF.

	g_x	g_y	g_z	T_x (G)	T_y (G)	T_z (G)
[111] Defect (LiF)	2.0105 ± 0.0015	$=g_x$	2.0017 ± 0.0002	19 ± 5	$=T_x$	1005.9 ± 0.1
H(LiF:Na)[a]	2.0115 ± 0.0025	$\approx g_x$	2.0013 ± 0.0005	75 ± 25	$\approx T_x$	961.0 ± 0.6
V_K(LiF)[b]	2.0227 ± 0.0010	2.0234 ± 0.0010	2.0031 ± 0.0010	59	59	887
V_K(NaF)[c]	2.0220	$\approx g_x$	2.0014	47	47	897.1
V_{KA}(NaF:Li)[d]	2.0219 ± 0.0002	2.0231 ± 0.0002	2.00205 ± 0.00005	0^{+7}_{-0}	0^{+7}_{-0}	$916.4^{+0.3}_{-0.1}$

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The observed ESR angular dependence has been fitted to the spin Hamiltonian

$$\mathcal{H}_{\mathrm{ESR}} = \beta_0 \vec{\mathrm{S}} \cdot \mathrm{g} \cdot \vec{\mathrm{H}}_0 + g_0 \beta_0 \vec{\mathrm{S}} \cdot \mathrm{T} \cdot \vec{\mathrm{I}} - \gamma_{\mathrm{F}} \vec{\mathrm{H}}_0 \cdot \vec{\mathrm{I}}.$$

This was performed by choosing basis states

$$\psi_{m_S, I, m_I} = |m_s\rangle |I, m_I\rangle$$

(for $|I, m_I\rangle$, the usual triplet and singlet states $I = 1, 0, m_I = \pm 1, 0, 0$ are formed from the two fluorine nuclei of the molecule) and choosing principal values of g and T to be g_x, g_y, g_z and T_x, T_y, T_z, where z is taken parallel to the molecular axis. Because of the 3-fold rotation symmetry of the lattice about the [111] axis, g and T possess axial symmetry such that $g_x = g_y$ and $T_x = T_y$. An 8×8 matrix was constructed and diagonalized and the allowed ESR transitions [$\Delta m_S = \pm 1; \Delta m_I = 0$] were determined and compared with experimental values at selected orientations of magnetic field. Because of the large number of F centers, present accurate measurements could not be made for the central lines ($m_I = 0$ transitions) near $g = 2$. The ESR constants so obtained are shown in Table I along with corresponding constants for other F_2^--type centers, V_K and H in LiF and V_K and V_{KA} in NaF.

The [111] defect has resolved "secondary splitting" (Fig. 1) arising from the hyperfine interactions with neighboring lattice nuclei. The nature of the splitting is complex since it is observed to depend upon both the nuclear-spin state of the molecule and the direction of the magnetic field with respect to the lattice. For the magnetic field parallel to the molecular axis, the low-field resonance line shows a partially resolved seven-line splitting while the high-field line is structureless. As the field is rotated toward the [110] axis, a three-line splitting with amplitude ratio 1:2:1 appears. As the magnetic field is rotated away from the [111] axis toward the [001] direction, the seven-line splitting fades out and then reappears. It is tempting to assign this structure to the six nearby fluorines (two of which are shown in Fig. 2). However, because of the complicated behavior, more than one set of equivalent lattice nuclei may contribute to the "secondary splitting." Since we plan to make an ENDOR study of this defect, we are postponing the analysis of this additional structure.

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†Alfred P. Sloan Fellow.

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LOCATION OF ELECTRON AND HOLE CARRIERS IN GRAPHITE FROM LASER MAGNETOREFLECTION DATA[*,†]

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Magnetoreflection experiments have been carried out on pyrolytic graphite using circularly polarized radiation from an infrared gas laser source. From a preliminary analysis of the data we find that the carriers at point K in the Brillouin zone are electrons rather than holes. Additional support for this conclusion is obtained from a reexamination of the cyclotron-resonance data of Galt, Yager, and Dail.

Some time ago graphite magnetoreflection data were obtained by Dresselhaus and Mavroides using unpolarized light from a conventional infrared source, and were used as the basis of their extensive band parameter determinations.[1] These measurements have been repeated and extended using circularly polarized radiation from a gaseous infrared laser source.[2] Because of the use of the laser, we have obtained greatly improved data—both in terms of signal-to-noise ratio and in the greater information available in the polarized data. In addition, the laser experiment is inherently a high-resolution experiment so that we observe the true line shape of the magnetoreflection resonances.

The use of lasers in this type of experiment is a relatively new application of lasers to solid-state spectroscopy. Although lasers have found widespread application in areas such as Raman spectroscopy and high-resolution studies of the various atomic and molecular levels which participate in laser action, less attention has been paid to high-resolution experiments in which the electronic levels can be swept through the optical resonances by means of an external perturbation. Our present studies indicate that this should be a fertile field for future investigations.

Our experiments were carried out using a 100-kG water-cooled Bitter solenoid. Samples were mounted in a helium Dewar with their c axes parallel to the applied field. The laser radiation was generated by a gaseous neon laser and was incident almost normal to the sample surface. By focusing to a small area of the sample, line broadening from magnetic field inhomogeneities was effectively eliminated. Circular polarization was obtained using a Fresnel rhomb. Because gold-coated mirrors were used in the laser resonator, a large number of lines oscillated simultaneously and a low-resolution monochromator was used to select out one of them.

An important feature of the laser system was a feedback loop utilizing a second detector to stabilize the laser output power. This was accomplished by varying the discharge intensity of the laser and enabled us to reduce to less than 0.5 % the normally severe intensity fluctuations common to gaseous infrared lasers. Further reduction in the effects of amplitude fluctuations was accomplished by using two Cu:Ge detectors in a balanced configuration and employing differential electronics.

In the experiment the reflectivity of the sample was measured at constant photon energy as a function of magnetic field, and data were obtained at a number of wavelengths ranging from 5.4 to 21.7 μ. Typical recorder traces obtained for the two senses of circular polarization[3] with one laser line are shown in Fig. 1.

The oscillations in the lower trace and in the low-field portion of the upper trace are due to interband transitions between the Landau levels which arise from the degenerate E_3 bands of graphite.[1] The selection rules[4] for these transitions are $N_{(\mathrm{v})} \to (N+1)_{(\mathrm{c})}$ for the upper trace and $N_{(\mathrm{v})} \to (N-1)_{(\mathrm{c})}$ for the lower trace, where N is the Landau-level index and the subscripts v and c refer to the valence- and conduction-band lev-