

tem to which the Ising model applies.⁹

In conclusion, we have proposed a new method for measuring long-range order and have applied it to a displacive transition of K_2ReCl_6 . The results are consistent with the predictions of an Ising model.

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¹O. W. Dietrich and J. Als-Nielsen, *Phys. Rev.* **153**, 711 (1967).

²R. H. Busey, H. H. Dearman, and R. B. Bevan, Jr., *J. Phys. Chem.* **66**, 82 (1962).

³J. D. H. Donnay and Gabrielle Donnay, *Crystal Data*

Determinative Tables (American Crystallographic Association, Oak Ridge, Tennessee, 1963), p. 955.

⁴H. G. Smith and G. E. Bacon, *J. Appl. Phys.* **37**, 979 (1966).

⁵R. G. S. Morfee, L. A. K. Staveley, S. T. Walters, and D. L. Wigley, *J. Phys. Chem. Solids* **13**, 132 (1960).

⁶J. Als-Nielsen and O. W. Dietrich, *Phys. Rev.* **153**, 717 (1967).

⁷For Brillouin-zone symmetry-point designations, see for example, G. F. Koster, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5.

⁸M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England, 1954).

⁹M. E. Fisher, in *Lectures in Theoretical Physics*, edited by Wesley E. Brittin (University of Colorado Press, Boulder, Colorado, 1965), Vol. VIII, p. 1-160.

ELECTRON-NUCLEAR DOUBLE-RESONANCE STUDY OF AN *H* CENTER IN LiF †*

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An electron-nuclear double-resonance study of the *H* center produced by x rays in reagent-grade LiF shows the defect to be a F_2^- molecule located on a single lattice site but associated with a Na^+ impurity. Attempts to produce isolated *H* centers in high-purity LiF have been unsuccessful.

The role of interstitials in radiation damage of alkali halides is not completely understood. The well-known *F* center¹ is an electron trapped at a halide-ion vacancy, but what becomes of the halide ion that is removed to form the vacancy is still an active research topic. Several years ago considerable information on interstitials was obtained by Känzig and Woodruff² in an electron-spin resonance (esr) study of the *H* center. They determined that this center was the equivalent of an interstitial halide atom but in the form of a negatively charged diatomic halide molecule (e.g., F_2^-) located on a single lattice site with the molecular axis oriented in a [110] crystalline direction (see Fig. 1). This Letter reports on an electron-nuclear double-resonance (ENDOR) study of the *H* center in LiF.

The esr of the *H* center in LiF is characterized by a large anisotropic hyperfine interaction between the unpaired electron spin and the two nuclei (labeled 1 and 2 in Fig. 1) of

the molecule. Since the fluorine nucleus has a spin of $\frac{1}{2}$, the esr spectrum consists of three lines corresponding to the three nuclear-spin states [$m_I(1, 2) = 0, \pm 1$] with a separation of about 960 G between the center line [$m_I(1, 2) = 0$] and the side lines [$m_I(1, 2) = \pm 1$]. This part of the spectrum is very similar to that of the self-trapped hole^{3,4} (V_K center). In addition, each line of the *H* center is split into a miniature version of the above splitting. This additional splitting is produced by the interaction with the two equivalent nuclei labeled 3 and 4 in Fig. 1. The separation between the center line [$m_I(3, 4) = 0$] and the side lines [$m_I(3, 4) = \pm 1$] is about 90 G. This additional structure was the main experimental evidence on which the model of the *H* center² was based.

The ENDOR spectrum of the *H* center is shown in Fig. 1. The principal-axis hyperfine constants of the ENDOR nuclei are listed in Table I. The *H* centers were produced by x rays in a reagent-grade LiF sample with a temper-

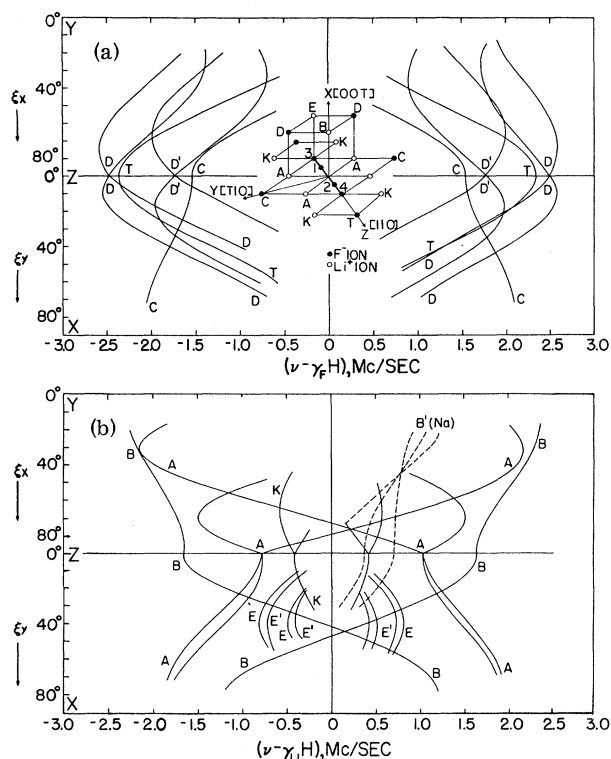


FIG. 1. (a) Lattice model and the angular dependence of the fluorine ENDOR lines. Data are plotted as $\nu(\text{exptl}) - \gamma H$. (b) Lithium and sodium ENDOR lines. The sodium lines are shown in their correct positions with respect to the lithium lines by plotting $\gamma_{\text{Na}}(\text{exptl}) - \gamma_{\text{Li}}H$.

ature of 90°K or lower. The ENDOR data were taken at about 40°K. Most of the data were taken on a high-field esr line [$m_I(1, 2) = -1$; $m_I(3, 4) = 0$]. Angular dependence studies were made for rotations about the two principal axes which are perpendicular to the molecular axis of the

defect. No data were taken for angles greater than 75° away from the molecular axis and none were taken for rotation about the molecular axis because the H -center esr lines for these positions are hidden by the much larger esr lines of the V_K center. Because of the anisotropy of the esr spectrum, data were taken at different magnetic fields so the field variation has been removed in Fig. 1 by plotting $\nu(\text{exptl}) - \gamma_n H$.

The surprising result is that the H center in LiF is indeed an F_2^- molecule located on a single lattice site but associated with a Na^+ impurity located at a nearest-neighbor site (one of the B sites). In addition to the sodium ENDOR lines, the splitting of line A for the y -axis rotation and the presence of two nonequivalent sets (E, E' ; D, D') would not occur if the F_2^- molecule were not associated with the Na^+ impurity. Additional data (not shown) were taken for rotation about an axis making a 60° angle with the molecular axis. These data showed a splitting of the line C which for symmetry reasons is a single line for the rotations in Fig. 1. The only expected splitting not experimentally observed is for the T nuclei on the molecular axis for the y -axis rotation. This can be understood by comparison with the V_{KA} center in NaF .⁵ There the F fluorine nuclei on the molecular axis show only a very small splitting. The T nuclei of the H center are more distant from the F_2^- molecule than are the F nuclei of the V_{KA} center. Therefore, the splitting permitted by symmetry is too small to be resolved.

The association of an interstitial with an impurity (Na^+) larger than the host ion (Li^+) is a surprise. Previous associations (e.g., F_A)^{6,7}

Table I. Principal-axis (x , y , and z) hyperfine constants in megacycles per second and orientations (α , β , and γ) with respect to the H -center principal axes (X , Y , and Z).

Nucleus	A_x	A_y	A_z	α (deg)	β (deg)	γ (deg)
A (Li)	-3.93 ± 0.04	4.34 ± 0.03	-3.00 ± 0.02	~ 1	23.5 ± 1.0	23.5 ± 1.0
B (Li)	2.48 ± 0.04	-4.87 ± 0.04	-3.29 ± 0.02	0	0	0
B (Na)	-3.05 ± 0.10	-6.05 ± 0.04	-5.39 ± 0.02	0	0	0
E (Li)	1.00 ± 0.03	...	-1.62 ± 0.03	46 ± 2	0	46 ± 2
E' (Li)	0.83 ± 0.03	...	-1.45 ± 0.03	46 ± 2	0	46 ± 2
K (Li)	-0.33 ± 0.12	-0.31 ± 0.12	1.15 ± 0.02	0	28 ± 1	28 ± 1
C (F)	-4.33 ± 0.04	1.06 ± 0.11	-3.07 ± 0.02	~ 1	~ 1	0
D (F)	-6.81 ± 0.90	2.18 ± 0.60	-5.10 ± 0.10	52 ± 2	53 ± 2	8 ± 2
D' (F)	-4.67 ± 0.90	2.38 ± 0.60	-3.92 ± 0.10	52 ± 2	54 ± 2	15 ± 2
T (F)	0.55 ± 0.08	0.54 ± 0.08	4.68 ± 0.02	~ 0	0	~ 0

and V_{KA} ⁵) of color centers with impurities have been with smaller impurities (e.g., Li^+ in sodium halides and Li^+ and Na^+ in potassium halides). Past attempts⁵ to produce an association between the self-trapped hole and Na^+ impurities in LiF have been unsuccessful.

Since an associated H center was not expected, the LiF crystals studies were not deliberately doped with Na^+ impurities. However, since attempts to produce H centers in high-purity Harshaw LiF were unsuccessful, the samples used were grown from reagent-grade material. Attempts⁸ have been made without success to produce H centers in high-purity LiF by x rays at 4.2°K and by bombardment with 4.5-MeV electrons at liquid-nitrogen temperatures (sample temperature less than 90°K during bombardment).

Since we have not produced the isolated H center without the presence of the Na^+ impurity in LiF, we plan to examine KCl where the production of the H center apparently occurs

in high-purity material.

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¹W. D. Compton and J. H. Schulman, *Color Centers in Solids* (The Macmillan Company, New York, 1962).

²W. Känzig and T. O. Woodruff, *J. Phys. Chem. Solids* **9**, 70 (1959).

³T. W. Woodruff and W. Känzig, *J. Phys. Chem. Solids* **5**, 268 (1958).

⁴R. Gazzinelli and R. Miehler, *Phys. Rev. Letters* **12**, 644 (1964).

⁵I. Bass and R. Miehler, *Phys. Rev. Letters* **15**, 25 (1965).

⁶F. Lüty, *Z. Physik* **165**, 17 (1961).

⁷R. Miehler, *Phys. Rev. Letters* **8**, 362 (1962).

⁸Measurements by Mr. Hou Chu, Purdue University (unpublished).

ELECTRONIC VOLUME EFFECT IN SILICON*

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Volume contraction of a silicon crystal under intense illumination by laser light has been observed and an explanation of the phenomenon in terms of an electronic effect is proposed.

The generation of elastic waves in solids and liquids due to the absorption of intense, short-duration light pulses available from Q-switched lasers has been discussed previously.¹ The energy of the light absorbed causes heating of a surface layer; because of thermal expansion a compression pulse is propagated into the sample. For a free surface, the boundary conditions require that the compression be followed by a tension pulse of equal magnitude.

In the present experiments, the laser consists of a neodymium-doped glass rod Q switched by a rotating prism to produce pulses of about 25-nsec full width at half-amplitude. For low-intensity light of this wavelength silicon has an absorption constant of $\alpha = 40 \text{ cm}^{-1}$. The laser output is monitored by a calibrated ITT FW-114 planar photodiode. The samples are cylindrical single crystals of phosphorus-doped n-type silicon of 30- to 50- Ω -cm resistivity,

with (111) faces lapped optically flat to 3 fringes and parallel to 30 secs. To measure the amplitude of the stress pulse that has traveled through the specimen, an X-cut quartz stress gauge, 1.3 cm in diameter and 0.6 cm thick, is bonded to the back face of the sample with a thin layer of Nonaq stopcock grease.² The piezoelectric current gives a record of stress with time, which is displayed on the oscilloscope. The operation and calibration of such stress gauges have been described by Graham, Neilson, and Benedick.³

In Fig. 1(a) is shown the shape of a typical laser pulse incident on the sample, as monitored by the photodiode, on a time scale of 40 nsec/cm. The resulting stress pulse registered by the quartz gauge is depicted in Fig. 1(b); the time scale is 200 nsec/cm and the gauge is oriented such that an upward deflection on the oscilloscope screen indicates tension, while down-