

Effect of Pressure on the Hyperfine Structure of F Centers in LiF*

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An electron-spin-resonance study at room temperature has been performed on F centers in LiF at hydrostatic pressures up to 4 kbar. An average value for the variation of the hyperfine constants with pressure is found to be $a^{-1}\partial a/\partial P = (2.4 \pm 1.1) \times 10^{-6} \text{ bar}^{-1}$. This result, when taken with the bulk compressibility of LiF, and the behavior with pressure of the optical transitions of F centers in alkali halides, gives moderately good agreement with the point-ion model of Gourary and Adrian.

INTRODUCTION

THIS paper reports the change in the hyperfine structure of the F center in LiF as a function of hydrostatic pressure. The interaction of the F electron with its surrounding ions evidences itself by causing a broad electron-spin-resonance (ESR) line with partially resolved structure.¹ These features are due almost entirely to the eight next-nearest-neighbor fluorine ions and the six nearest-neighbor lithium ions. Although it is possible to study each of the various neighbors separately through the use of the electron-nuclear double-resonance (ENDOR)² technique, this approach was postponed and only an average value representing mostly the isotropic-fluorine hyperfine interaction is given.

EXPERIMENTAL DETAILS AND RESULTS

Harshaw single-crystal LiF was formed into the shape of a torus with an ultrasonic impact grinder. It was then given a 150-megarad irradiation at 0°C by an electron beam. The crystal turned a dark green color owing to an electron excess center, unstable at room temperature,

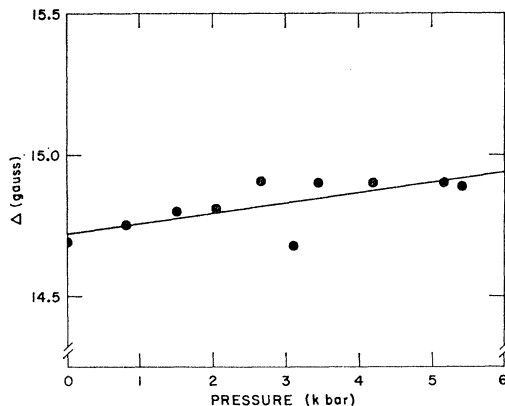


FIG. 1. The variation of the hyperfine splitting with pressure.

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¹ W. C. Holton, H. Blum, and C. P. Slichter, *Phys. Rev. Letters* **5**, 197 (1960); W. C. Holton and H. Blum, *Phys. Rev.* **125**, 89 (1962).

² G. Feher, *Phys. Rev.* **105**, 1122 (1957).

which has a g value slightly greater than 2. This center disappears overnight leaving only the F center and some M -center concentration. The F -center concentration was a little low so the crystal treatment was extended by an irradiation at room temperature with 40-keV x rays for a few hours. It was then inserted into an X-band coaxial microwave cavity within a high-pressure bomb.³ The [111] crystal axes were along the external magnetic field. The high pressure press employed was one of Bridgman's. The pressure was monitored by measuring the resistance of a coil of manganin wire which was calibrated at the freezing point of mercury at 0°C.⁴

The results, shown in Fig. 1, can be expressed with a least-squares fit to the data as

$$\Delta^{-1}(\partial\Delta/\partial P) = (2.4 \pm 1.1) \times 10^{-6} \text{ bar}^{-1}, \quad (1)$$

where Δ is the average separation of two of the hyperfine lines. The point at 1 bar is from the work of Ref. 1. The ESR spectra there are also taken at room temperature. Using the compressibility data for bulk LiF from Bridgman,⁵ we find

$$\partial \ln \Delta / \partial \ln R = f^{-1} (4.8 \pm 2.2), \quad (2)$$

where f is the ratio of the effective local compressibility to the bulk compressibility. Extrapolation of results of studies of the frequency shift of the F band with pressure,⁶ for other alkali halides, compared with the Ivey relation⁷ gives us an approximate value of $f_{\text{optical}} = 2$. The shift of the F band in LiF with pressure has not yet

³ The cavity and bomb designs are equivalent to those of Walsh [W. M. Walsh and N. Bloembergen, *Phys. Rev.* **107**, 904 (1957)]. The spectrometer is the one used by H. Blum and G. B. Benedek, *Bull. Am. Phys. Soc.* **8**, 619 (1963).

⁴ D. H. Newhall, L. H. Abbot, and R. A. Dunn, Annual Meeting ASME, Paper 62-WA-283, 1962 (unpublished).

⁵ P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **70**, 285 (1935). The value for the compressibility quoted in P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, Ltd., London, 1949) is in error. We are using the expression $-\Delta V/V = 15.05 \times 10^{-7} P - 5.4 \times 10^{-12} P^2$ with P in bars. This includes the corrections of Ref. 4. See also S. Mayberg, *Phys. Rev.* **79**, 375 (1950).

⁶ I. S. Jacobs, *Phys. Rev.* **93**, 993 (1954); R. A. Eppler and H. G. Drickamer, *J. Chem. Phys.* **32**, 1418 (1960); S. Minomura and H. G. Drickamer, *ibid.* **33**, 290 (1960); W. G. Maisch and H. G. Drickamer, *J. Phys. Chem. Solids* **5**, 328 (1958); H. Knof and W. G. Maisch, *ibid.* **24**, 1625 (1963).

⁷ H. F. Ivey, *Phys. Rev.* **72**, 341 (1947).

been measured because that band lies outside the frequency range of the high-pressure optical systems.

DISCUSSION

One can predict with moderate success the hyperfine structure of the F electron by employing the modified Heitler-London model of Gourary and Adrian⁸ where the F electron envelope wave function Ψ is calculated for an electron in the crystalline electrostatic field of the surrounding ions. In order to satisfy the Pauli principle this wave function is then perturbed in such a way that the overlap with the closed ion cores is reduced to zero; that is

$$\Psi_F = N \left[\Psi - \sum_{\alpha j} (\Psi | \Phi_{\alpha j}) \Phi_{\alpha j} \right], \quad (3)$$

where $\Phi_{\alpha j}$ is the α th atomic state of the j th ion and N is the normalization constant

$$N = \left[1 - \sum_{\alpha j} (\Psi | \Phi_{\alpha j})^2 \right]^{-1/2}. \quad (4)$$

The contact hyperfine interaction with a nucleus α at R_α can be written

$$a_\alpha = (16\pi/3)\beta(\mu_\alpha/I_\alpha) |\Psi_F(R_\alpha)|^2, \quad (5)$$

where β is the Bohr magneton, μ_α the magnetic moment and I_α the spin of the nucleus.

With a certain number of simplifying assumptions treated in some detail by Adrian and coworkers^{8,9} concerning the nature of the various atomic wave functions, one can rewrite Eq. (5)

$$a_\alpha = (16\pi/3)\beta(\mu_\alpha/I_\alpha) |\Psi(R_\alpha)|^2 A_\alpha, \quad (6)$$

where A_α , the so-called enhancement factor, is a parameter depending only on the free ionic wave

⁸ B. S. Gourary and F. J. Adrian, in *Solid State Physics*, edited F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10, p. 127.

⁹ B. S. Gourary and A. E. Fein, Westinghouse Research Laboratories, Scientific Paper 129-V000-P1, 1961 (unpublished); F. J. Adrian, *J. Chem. Phys.* **32**, 972 (1960).

function. For LiF, Gourary and Adrian predict $A(\text{fluorine})_{\text{theory}} = 350$; whereas ENDOR measurements¹ give $A(\text{fluorine})_{\text{experiment}} = 200$.

The effect of pressure in this model is twofold. The functional dependence of Ψ changes with interionic radius. This happens because the crystalline electrostatic field in which the F electron finds itself is a function of the positions of the ions. R_α also decreases with pressure. With the Gourary and Adrian type-III wave function¹⁰

$$(\partial \ln a / \partial \ln R) = (\partial \ln \Psi^2 / \partial \ln R) = -3. \quad (7)$$

Equation (7) assumes that the variational parameters in the type-III wave function remain constant as the interionic radius changes. This is, in fact, not a bad assumption for LiF. Combining Eq. (7) with Eq. (2) we find that $f_{\text{ESR}} = 1.6$ compared with the semiempirical $f_{\text{optical}} = 2$ inferred from optical data. The errors associated with these determinations and the roughness of the available models used allow us to claim reasonably good agreement between the numbers. We conclude that the Gourary and Adrian point-ion model is as reliable in predicting the pressure variation in the hyperfine structure as it is in predicting the value at atmospheric pressure.

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¹⁰ See Ref. 8, p. 229.