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ELECTRON-NUCLEAR DOUBLE RESONANCE STUDY AND EXCHANGE POLARIZATION OF THE SELF-TRAPPED HOLE IN LiF†*

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This Letter discusses the results of a detailed electron nuclear double resonance (ENDOR) study of the self-trapped hole in LiF. In addition to a verification of the accepted model of the self-trapped hole, the experimental hyperfine constants of the lattice nuclei provide a measure of the large exchange polarization of closed electron shells at points distant from the nuclei of a simple molecule.

The self-trapped hole in alkali halide crystals was discovered by Känzig[1] in an electron spin resonance (ESR) investigation of KCl x rayed at liquid nitrogen temperature. This defect was called the V_K center, and detailed ESR studies were made in different materials by Känzig and co-workers.[2,3] Also, optical studies were made by Delbecq and co-workers.[4] Both the ESR and optical data were analyzed in terms of a negatively charged diatomic molecule, e.g., F_2^-, oriented along a [110] axis of the crystal (i.e., the hole is shared by two halide ion lattice sites).

The ESR of the V_K center is characterized by a large, anisotropic hyperfine interaction between the unpaired electron and the two nuclei of the molecule. Since the fluorine nucleus has a spin of $\frac{1}{2}$, the ESR of F_2^- consists of three hyperfine lines ($m_I[\mathrm{F}]=\pm1,0$) with a separation between the $m_I[\mathrm{F}]=\pm1$ lines of about 1800 gauss when the magnetic field is parallel to the molecular axis and a separation of about 150 gauss when the field is perpendicular to the axis. The single resonance lines in LiF are about 12 gauss wide due to unresolved hyperfine interactions with the surrounding nuclei of the lattice.

The detailed ENDOR results for the V_K center are shown in Fig. 1. Because of the low symmetry at most of the neighboring nuclear sites, it was necessary to determine the angular dependence of the ENDOR lines for rotations about the three principal axes of the defect. Identification

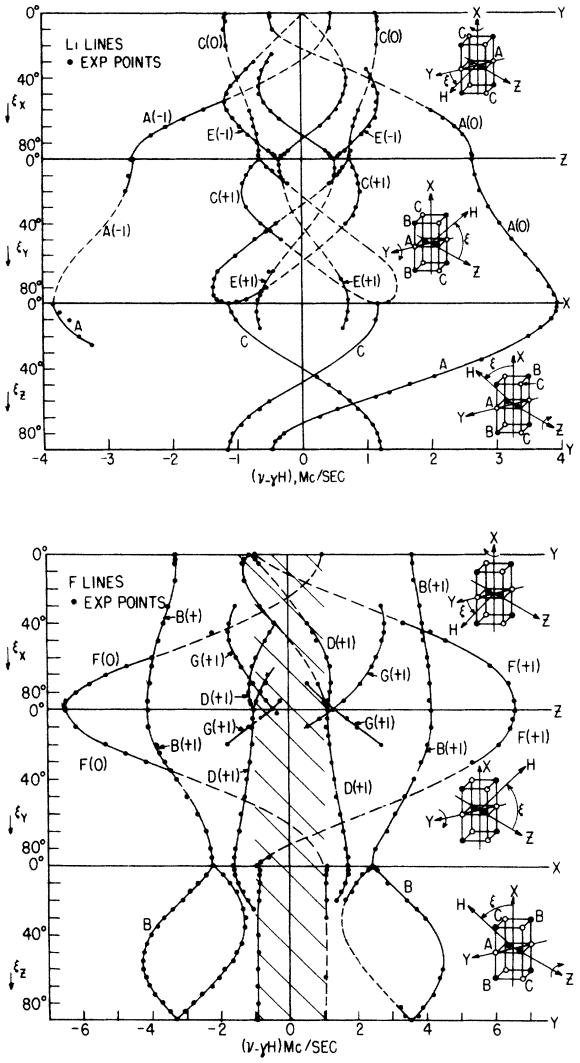

FIG. 1. Angular dependence of ENDOR lines for V_K center. Letters indicate the nuclear group and (±1), (0) indicate the single resonance line ($m[\mathrm{F}]=\pm1,0$) for which the data were taken. Because the magnetic field is a function of crystal orientation for the $m[\mathrm{F}]=\pm1$, the ENDOR data are plotted as $\nu-\gamma H$.

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

Nucleus	A_x (Mc/sec)	A_y (Mc/sec)	A_z (Mc/sec)	α	β	γ
A (Li)	-7.78	+0.97	-5.36	0°	0°	0°
B (F)	-2.75	-8.69	-8.17	34°	34°	0°
C (Li)	+2.70	-2.34	-1.80	17°	0°	17°
D (F)	-3.37	+2.70	-2.36	0°	10°	10°
E (Li)	-1.43	-1.40	+2.35	0°	35°	35°
F (F)	-1.98	-1.98	+13.05	0°	0°	0°

of the ENDOR lines can be made by considering whether the nuclei of a given group (indicated in the figures as A, B, C, etc.) are equivalent or nonequivalent for the different rotation axes. This identification gives perfect agreement with the V_K model and no other model could be found that would explain the results.

The nuclear principal-axes hyperfine constants for six groups of nuclei are given in Table I along with the orientations of the nuclear principal axes with respect to the principal axes of the V_K center. The signs of the hyperfine constants were determined by assuming that the angular dependence is due to the dipole-dipole interaction between the nuclei and the unpaired electron. The isotropic contact part of the hyperfine interaction is $a_C = \frac{1}{3}(A_X + A_Y + A_Z)$. The experimental a_C values are listed in the second column of Table II.

The unpaired spin of the F_2^- molecule is in a σ_u molecular orbit.[2,5] A single contour of the electron density of the σ_u orbit is represented in Fig. 2(b) as two $2p$ atomic orbits. Because the center of the molecule is a point of inversion symmetry for the entire lattice, the X-Y plane (containing nuclear groups A and B) will be a nodal plane for the "true" σ_u orbit. A plane containing the C and D nuclei will not be an exact nodal plane because of the relaxation of the F_2^- molecule and because of S atomic orbital admixture into σ_u.

However, it will be noticed in Table II that the

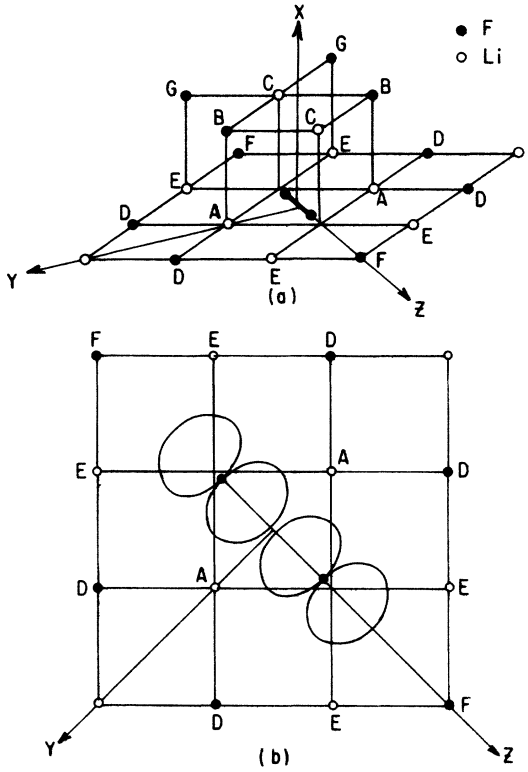

FIG. 2. (a) Local geometry of the V_K center and lettering of equivalent nuclear groups. (b) The unpaired spin is in a σ_u molecular orbit represented here as two $2p$ atomic orbits.

Table II. Comparison of calculated contact part of hyperfine interactions with experimental values.

Nucleus	a_c(exp)	a_c(unpol)	a_c(pol)	Percent polarization of $\lvert\psi(r_n)\rvert^2$
A (Li)	-4.14	0.0	-4.7	σ_g, 15.9; π_u, 14.8
B (F)	-6.54	0.0	-4.6	σ_g, 29 ; π_u, 25.4
C (Li)	-0.48	+0.2	-1.6	π_u and π_g, 19.5
D (F)	-1.01	+0.2	-2.4	π_u and π_g, 29.3
E (Li)	-0.16	+1.8	+0.4	σ_u and σ_g, 23.6; π_u and π_g, 23.8
F (F)	+3.03	+2.7	+1.4	σ_u and σ_g, 30.6

A and B nuclei in the σ_u nodal plane have large, negative contact interactions, i.e., the spin density, $|\psi(r_n)|^2$, on a given nucleus points in a direction opposite to that of the unpaired σ_u electron. There are at least four mechanisms that could produce a nonzero contact interaction for the A and B nuclei.

(1) If the center of the molecule were not a point of inversion symmetry, then the X-Y plane would no longer be a rigorous nodal plane of σ_u. The only mechanism that could destroy the inversion symmetry and still be consistent with the rest of the ENDOR data would be lattice vibrations. There should then be a temperature dependence of this interaction. Measurements at 20°K and 77°K show no temperature independence greater than the experimental accuracy of ±0.3%.

(2) The g shift of the V_K center has been explained[2] as due to the spin-orbit coupling mixing some π_u orbit with the σ_u. Since the X-Y plane is not a nodal plane of the π_u orbit, this could result in a nonzero spin density at the A and B nuclei. However, the amount of the π_u admixture is known from the experimental g shift. The resulting spin density is two orders of magnitude too small.

Negative contact interactions due to exchange polarization of closed S shells are known to occur for the nuclei of magnetic ions and atoms in gases and solids.[6,7] Similar effects are also observed in free radicals.[8] There are two ways for exchange polarization to contribute to the contact interaction of the lattice nuclei.

(3) There will be an overlap of the σ_u orbit with the surrounding ions even if the spin density goes to zero at the nuclei. The ions will be polarized by the exchange interaction with the overlapping spin density. An order-of-magnitude estimate of this effect can be made by assuming that the polarization is proportional to the amount of overlap. It is known that divalent transition ions have a negative contact interaction roughly proportional to the number of unpaired d electrons.[6] Also, Shulman[9] has observed a negative contact interaction for F nuclei in K_2NaCrF_6. The amount of $2p$ character of the unpaired spin on the F^- ion as determined from the anisotropic part of the fluorine nuclear resonance was 4.9%. The exchange polarization contact interaction for the fluorine atom is 149 megacycles per second.[7,10] Therefore, a crude guess of the exchange polarization of the F^- ions in K_2NaCrF_6 would be 7.3 megacycles per second; Shulman observed 9.9 megacycles per second. However, this mechanism cannot explain the observed a_C values for the V_K center. For instance, the A lithium nuclei have $a_C = -4.14$ megacycles per second, whereas the experimental contact interaction for the lithium atom in the $(1s)^2 2p$ state is 10.5 ± 0.3 megacycles per second.[11] The other contact values are also too large to explain by overlap polarization.

(4) The following mechanism gives the correct order-of-magnitude explanation of the a_C values in Table II. At least one of the "closed shell" $2p$-type orbitals (σ_g, π_u, and π_g) will have nonzero values of $|\psi(r_n)|^2$ at all of the surrounding lattice nuclei. If these orbitals are polarized by an exchange interaction with the unpaired σ_u electron there will then be a nonzero (in most cases negative) spin density at all nuclei.

A crude estimate of this effect has been made using the following approximations. The σ_u molecular orbit is constructed from $2p$ atomic orbits neglecting overlap normalization. The radial part of $\psi(2p)$ is taken as that of the F^- ion.[12] The amount of polarization of $|\psi(\sigma_u)|^2$ at a given nuclear site is taken as one half the polarization of the fluorine atom at the same value of $|\psi(\text{atom})|^2$, as predicted by the unrestricted Hartree-Fock calculation.[7] Then the values of Gourary and Adrian[13] for orthogonalizing a plane wave to the closed ion shells are used. The internuclear distance for the F_2^- molecule is not known experimentally and was taken as 4.7 atomic units from the theoretical work of Das, Jette, and Knox.[14] Relaxations of other nuclei were neglected. Column three of Table II gives the positive contact interaction due to σ_u if exchange polarization is neglected. Column four gives the predicted a_C values with exchange polarization. In addition to giving a correct order of magnitude for the negative a_C values of the A, B, C, and D nuclei, a small a_C value is predicted for the E nuclei which are in a favorable position for a large overlap with σ_u. An improvement on the crude assumptions used in this calculation would require a detailed treatment of each of the points discussed above; nevertheless, the polarization of the "closed shell" molecular orbits seems to be the physical origin of the observed a_C values.

Column five of Table II gives the percentage of polarization at the nuclear sites. These values are much larger than the polarization of $|\psi(0)|^2$ that is usually observed at the nucleus of a magnetic ion. Indeed, the unrestricted Hartree-Fock[7] calculations predict a sign reversal in the net spin density of the fluorine atom at large values of radius. It is believed that the a_C values

determined in this experiment indicate that such large polarizations at large distances do occur.

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EXCITATION OF THE $2p$ STATE OF HYDROGEN BY ELECTRONS OF NEAR-THRESHOLD ENERGY*

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Recent experimental work in several atomic gasses[1-4] indicates that cross sections for excitation of optically allowed transitions by electron impact show a gradual rise from zero at threshold. For electric quadrupole transitions, the cross sections rise more sharply and reach a finite value at or very near threshold. In the case of atomic hydrogen, the near-degeneracy of the $2s$ and $2p$ states suggests that the $2s$ and $2p$ excitation functions might exhibit a superposition of these characteristics. Damburg and Gailitis[5] calculated the excitation cross sections of the $2s$ and $2p$ states of hydrogen in a $1s$-$2s$-$2p$ close-coupling approximation and found values near threshold which do not tend to zero. We have studied experimentally the threshold region of the cross section $Q_\perp$ for electron impact production of Lyman-α photons (1216 Å) from the $2p$-$1s$ transition in atomic hydrogen. We find that the cross section rises very steeply to a maximum, decreases to a minimum in about 0.3 eV, and then rises to a broad maximum.

The experiment was carried out in a differentially pumped high-vacuum crossed-beam apparatus. Hydrogen was thermally dissociated in a tungsten oven at 2500°K. The evolved H beam had a density of $\sim 10^9$ cm^{-3} at the interaction region. The ~1.5-μA electron beam was produced by a high-perveance electrostatic gun with axial symmetry. A Soa-type acceleration stage[6] was followed by a decelerating lens which focused the electrons into a field-free reaction space. Entrance and exit apertures assured that the electron beam trajectories passed through the 1-cm-wide atom beam. About 2% of the current passed into a hemispherical retarding analyzer,[6] which had a design resolution, $\Delta E/E$, of 0.25%. The electron energy distribution was measured at 10 eV by a modulated retarding potential technique.[7] The distribution, uncorrected for analyzer resolution, had a width at half-maximum of 0.35 eV and could be accurately represented by $dI/d\chi = 475 I\chi^2 e^{-9.83\chi}$, where I is the total electron current and χ is the energy in eV above