band, and the B exciton from the Γ_9 band. Since spin-spin splittings and the valence band spin-orbit splitting are all small compared to the exciton binding energies (about 0.059 eV[1]), it follows that the Γ_7 band lies about 0.005 eV above the Γ_9 band. The existence of two polariton absorption lines has completed the observation of the set of level crossings which can occur. The absence of absorption at the transverse exciton energies in the "wrong" mode is now seen to be a simple consequence of the importance of polariton effects.

The existence of polariton absorption lines with $H \parallel \vec{q}$ is a classical effect in anisotropic crystals. The fact that such lines appear even in the absence of magnetic fields and masquerade with or without a field as weak absorption lines, displaced from the transverse exciton states they have replaced, makes them a nontrivial feature of optical investigations of anisotropic crystals.

We wish to thank R. T. Lynch and E. D. Kolb for supplying the ZnO crystals.

---

[1] D. G. Thomas, J. Phys. Chem. Solids 15, 86 (1960).

[2] J. J. Hopfield, J. Phys. Chem. Solids 15, 97 (1960).

[3] Y. S. Park, C. W. Litton, T. C. Collins, and D. C. Renolds, Bull. Am. Phys. Soc. 10, 331 (1965).

[4] J. J. Hopfield and D. G. Thomas, J. Phys. Chem. Solids 12, 276 (1960). The numbers given as β on p. 280 of this reference are in fact values of $4\pi\beta$.

[5] D. C. Reynolds, C. W. Litton, and T. C. Collins, Bull. Am. Phys. Soc. 10, 331 (1965).

[6] J. J. Hopfield and D. G. Thomas, Phys. Rev. 132, 563 (1963).

[7] See, for example, Robert S. Knox, Theory of Excitons (Academic Press, Inc., New York, 1963), p. 133.

ELECTRON-NUCLEAR DOUBLE RESONANCE STUDY OF THE SELF-TRAPPED HOLE ASSOCIATED WITH LITHIUM IN NaF*

Isaac L. Bass and Robert Mieher†

Columbia Radiation Laboratory, Columbia University, New York, New York

(Received 27 May 1965)

Electron spin resonance (esr) and electron-nuclear double resonance (ENDOR) studies have shown that self-trapped holes (V_K centers) in NaF doped with lithium associate with the Li ions. This complex, in addition to being a new color center, is of interest because of the close resemblance of its esr spectrum to that of the center in LiF identified by Känzig[1,2] as the antimorph of the F center (V_F center).

The esr[3,4] and optical properties[5] of the V_K center have been investigated in several alkali halides. These studies led to the molecule-ion model in which the hole is shared by two adjacent halide ions to form a negatively charged diatomic molecule, e.g., F_2^-, oriented along a [110] crystalline axis. An ENDOR study of the V_K center in LiF by Gazzinelli and Mieher[6] has provided definite verification of this model. A similar ENDOR study has been made of the V_K center in NaF.[7]

In this Letter, the name V_{KA} center will designate the complex consisting of a V_K center associated with an alkali impurity.[8] The lithium V_{KA} center in NaF, which is the subject of this Letter, is shown schematically in Fig. 1.

These centers are produced in crystals grown from a melt of reagent-grade NaF doped with ≈1% LiF by weight. A sample is x irradiated (50 kV, 30 mA, ≈24 hr) at 77°K to produce V_K centers. Upon warming, the onset of conversion to V_{KA} centers is observed at ≈140°K, and the conversion is complete at ≈160°K. The V_{KA} centers are stable at 160°K. No trace of the V_K-center esr remains upon recooling to 77°K. The conversion efficiency based on esr amplitude ratios appears to be near 100%. Attempts were made to orient the V_{KA} centers by optical methods which were successfully used to orient V_K centers in NaF and LiF. However, the V_{KA} centers were dissociated with a consequent regeneration of V_K centers.

The V_{KA}-center esr spectrum, like that of the V_K center in the alkali fluorides, is characterized by a large, anisotropic hyperfine interaction between the unpaired electron and the two nuclei of the molecule. There are, in general, four esr lines corresponding to the four possible combinations of the spins of the two fluorine nuclei ($m_I[\mathrm{F}] = \pm 1, 0, 0$). The separation between the $m_I[\mathrm{F}] = \pm 1$ lines is ≈1800 G

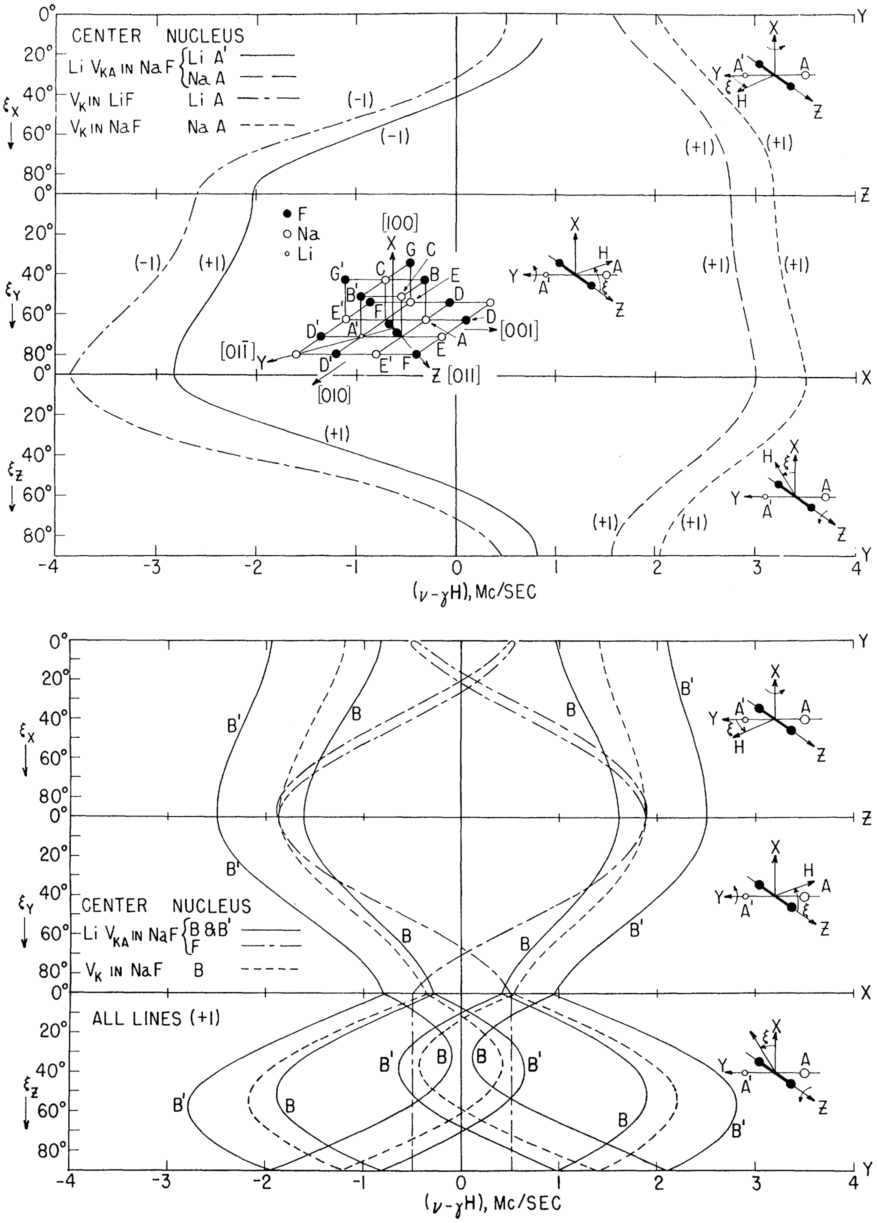

FIG. 1. Comparison of angular dependence of some ENDOR lines of lithium V_{KA} center in NaF with corresponding lines of the V_K centers in NaF and LiF. Geometry of V_{KA} center and lettering of nuclear groups is shown as inset in top figure. Labels (±1), (0) indicate esr line (m_I[F] = ± 1,0) for which data were taken. Because the magnetic field is a function of crystal orientation for m_I[F] = ± 1, the ENDOR data are plotted as $\nu - \gamma H$. Well-resolved quadrupole triplets of the sodium nuclei were observed; for clarity only the central line is shown. Also, only one of the pair of ENDOR lines ($m_S = \pm\frac{1}{2}$) are shown for the alkali nuclei.

when the field is parallel to the molecular axis and is ≈150 G when perpendicular. The nonequivalence of the molecular fluorines of the V_{KA} center produces an observable separation of the m_I[F] = 0 lines for field orientations where they would be unresolved for the V_K center. The separation is ≈18 G when the field is in the yz plane and makes a 45° angle with the molecular axis. These features of the esr angular dependence are shown in Fig. 2. The esr lines are designated both by the conventional labels[4] R_1, R_2, R_3, R_4, and by the symbols (±1), (0), which indicate the nuclear spin state m_I[F]. The esr linewidth of both the V_K cen-

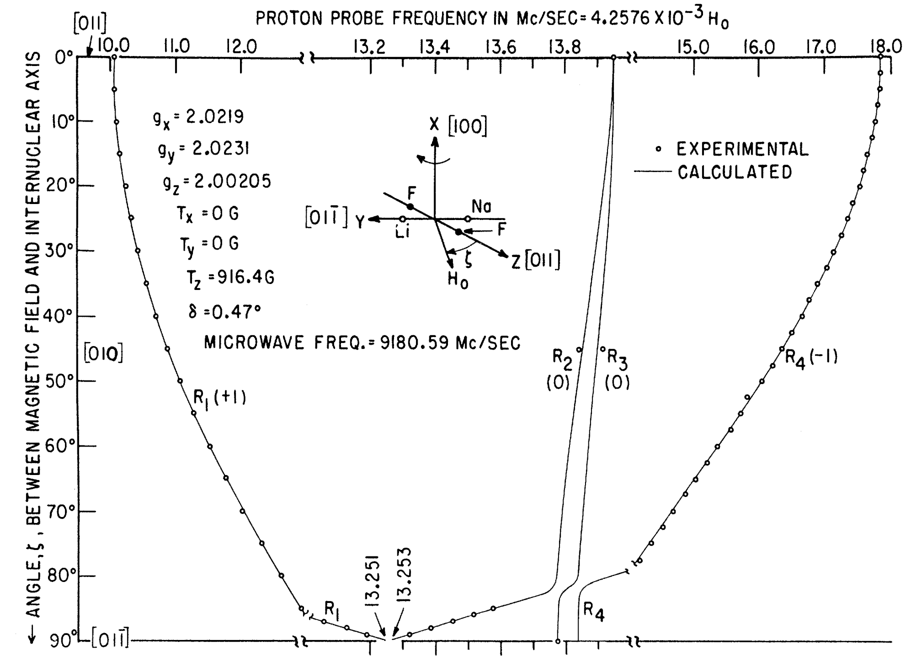

FIG. 2. Experimental and calculated angular dependence of the four esr lines of the lithium V_{KA} center in NaF. The magnetic field is rotated in the plane of the bent bond. The central portion of the magnetic-field axis has been expanded in order to show the splitting of the R_2 and R_3 lines caused by the bent bond.

ter and the lithium V_{KA} center in NaF is ≈9 G, and is due to unresolved hyperfine interactions with the surrounding nuclei of the lattice. The molecular fluorine hyperfine tensors of the V_{KA} center, like those of the V_K center, are axially symmetric within experimental uncertainty, but unlike those of the V_K center, their symmetry axis is not parallel to a line between the two molecular nuclei (to be thought of as a "bent bond"). The principal value of these tensors, the angle between their symmetry axes and the internuclear axis ("bond angle"), and the principal values of the g tensor are given in Table I for the lithium V_{KA} center and V_K center[9] in NaF, and for the V_F center[1,2] and V_K center[9] in LiF. The bond angle used in Fig. 2 was selected so that the calculated curve fits the experimental $R_3(90°)$ line position.

The most significant ENDOR results of the V_{KA} center are shown in Fig. 1. Angular dependences are given for field rotations about the x, y, and z coordinate axes. Complete angular dependences could be obtained only from the R_1 and R_4 esr lines because we were unable to orient the V_{KA} centers optically. Identification of an ENDOR line with a particular nucle-

Table I. Principal values of the g tensors, principal values of the molecular-fluorine hyperfine tensors (in gauss), and the bond angles (δ) of the lithium V_{KA} center and the V_K center in NaF, and of the V_F center and V_K center in LiF.

Crystal	Center	g_x	g_y	g_z	$\lvert T_x\rvert$ (G)	$\lvert T_y\rvert$ (G)	T_z (G)	δ
NaF	Li V_{KA}	2.0219 ±0.0002	2.0231 ±0.0002	2.002 05 ±0.000 05	≤7	≤7	$916.4^{+0.3}_{-0.1}$	0.6 ±0.2°
	V_K[a]	2.0220	2.0220	2.0014	47	47	897.1	
LiF	V_F[b]	2.023 ±0.002	2.023 ±0.002	2.001 ±0.002	≈0	≈0	915	≈4°
	V_K[a]	2.0239	2.0239	2.0034	57	57	883.7	

[a] Reference 9.

[b] Reference 1 and 2.

ar group (indicated in the figure as A, A', B, B', C, etc.) is made on the basis of equivalence or nonequivalence of nuclei within the group for different field orientations. Comparison of angular dependences with those of the V_K centers in NaF and LiF also facilitates this identification. Several of these comparisons are shown in Fig. 1. Hyperfine-tensor principal values and principal-axis orientations are given in Table II for eight different nuclear groups of the V_{KA} center and several groups of the V_K centers in NaF and LiF. The signs of the principal values are chosen so that most of the contact interactions are negative as discussed by Gazzinelli and Mieher.[6]

The following are the important ENDOR results which verify the V_{KA}-center model. The pair of ENDOR lines (corresponding to the two-electron spin states, i.e., $m_S = \pm\frac{1}{2}$) of the lithium A' nucleus were observed and were centered about $\gamma_{\text{Li}}H$. Comparison of its angular dependence (Fig. 1) with that of the lithium A nucleus of the V_K center in LiF indicates that its position is the A' lattice site. No other lithium ENDOR lines were observed. The ENDOR lines of the sodium A, C, E, and E', and the fluorine B, B', D, D', F, G, and G' nuclei were identified. In every instance the angular dependence is completely consistent with the symmetries of the center. Of especial significance is the fact that the ENDOR lines of the two F nuclei only split into two for the field rotation about the x axis (Fig. 1). The ENDOR lines of the primed and unprimed nuclear groups were found and compared with the corresponding group of the V_K center in NaF. Such a comparison is shown in Fig. 1 for the B-type nuclei. In order to distinguish between the primed and unprimed lines, two assumptions are made. One is that the primed nuclei and the molecule-ion relax toward each other into the A' lattice site. The other is that the contact interaction decreases with increasing distance from the molecule-ion. The results shown in Fig. 1 for the B-type and sodium A-type nuclei are consistent with these assumptions (as are results, now shown, for the D-type nuclei).

The existence of the lithium V_{KA} center in NaF suggests the possibility that the V_F-center esr spectrum observed by Känzig[1,2] in LiF was, in fact, produced by a V_{KA} center or a V_K center associated with some nonalkali impurity or defect. Unsuccessful attempts were made to observe a sodium V_{KA} center in LiF doped with Na. The complete conversion of the esr spectrum to what appears to be a lithium V_{KA} center in KCl doped with Li was observed, but an ENDOR study has not been made. This might indicate that association only occurs when the impurity is smaller than the host ca-

Table II. Principal-axis (x,y,z) hyperfine values in megacycles per second and orientations (α,β,γ) with respect to the molecule-ion principal axes (X,Y,Z) for all observed nuclei (except E, E', G, and G') of the lithium V_{KA} center in NaF and some nuclei of the V_K centers in NaF and LiF.

Crystal	Center	Nucleus	A_x (Mc/sec)	A_y (Mc/sec)	A_z (Mc/sec)	α	β	γ
NaF	Li V_{KA}	A(Na)	-6.15 ± 0.04	-3.17 ± 0.04	-5.50 ± 0.04	0°	0°	0°
NaF	V_K[a]	A(Na)	-7.00	-4.04	-6.42	0°	0°	0°
NaF	Li V_{KA}	A'(Li)	-6.04 ± 0.02	$+1.65\pm0.02$	-4.06 ± 0.02	0°	0°	0°
LiF	V_K[b]	A(Li)	-7.95	$+0.97$	-5.36	0°	0°	0°
NaF	Li V_{KA}	B(F)	$+1.34\pm0.06$	-3.945 ± 0.02	-3.22 ± 0.02	38.7±0.5°	38.7±0.5°	0°
NaF	V_K[a]	B(F)	$+0.85$	-4.39	-3.74	34°	34°	0°
NaF	Li V_{KA}	B'(F)	-0.22 ± 0.06	-5.85 ± 0.02	-5.01 ± 0.02	32.2±0.5°	32.2±0.5°	0°
NaF	Li V_{KA}	C(Na)	$+2.20\pm0.50$	-1.55 ± 0.10	-1.10 ± 0.10	≈15°	≈7.5°	≈15°
NaF	Li V_{KA}	D(F)	-1.36 ± 0.02	$+2.52\pm0.08$	-1.10 ± 0.04	0°	16.3±1.5°	16.3±1.5°
NaF	Li V_{KA}	D'(F)	-2.77 ± 0.02	$+3.35\pm0.08$	-1.73 ± 0.04	0°	10±2°	10±2°
NaF	Li V_{KA}	F(F)	-1.06 ± 0.04	-1.06 ± 0.04	$+3.77\pm0.02$	0°	2.5±0.5°	2.5±0.5°

[a] Reference 7.

[b] Reference 6.

tion. If so, the small ionic radius of Li$^+$ lends support to Känzig's interpretation of a V_K center associated with a cation vacancy. Comparison of bond angles (Table I) indicates that the molecule-ion of the V_F center in LiF is more strongly perturbed by association than the molecule-ion of the lithium V_{KA} center in NaF. A vacancy might be expected to produce a larger bond angle than a cation impurity. It is also interesting to note the near equality of the molecular-fluorine hyperfine constants for the two associated centers and to compare them with the values for the V_K center (Table I). The F_2^- bond length has apparently relaxed to nearly the same value for both the V_{KA} center and V_F center. Although the V_{KA}-center results appear to strengthen the V_F-center interpretation of Känzig's observations, they also make a more definite confirmation desirable.

---

*This work was supported in part by the National Science Foundation under Grant No. NSF-GP 3385 and in part by the Joint Services Electronics Program (U. S. Army, U. S. Navy, and U. S. Air Force) under Contract No. DA-28-043 AMC-00099(E).

†Alfred P. Sloan Foundation Fellow.

[1] W. Känzig, Phys. Rev. Letters 4, 117 (1960).

[2] W. Känzig, J. Phys. Chem. Solids 17, 80 (1960).

[3] T. G. Castner and W. Känzig, J. Phys. Chem. Solids 3, 178 (1957).

[4] T. O. Woodruff and W. Känzig, J. Phys. Chem. Solids 5, 268 (1958).

[5] C. J. Delbecq, W. Hayes, and P. H. Yuster, Phys. Rev. 121, 1043 (1961).

[6] R. Gazzinelli and R. Mieher, Phys. Rev. Letters 12, 644 (1964).

[7] Unpublished work by D. Daly. A report has been given in the Columbia Radiation Laboratory Seventh Quarterly Progress Report, September 15, 1964 (unpublished), p. 43.

[8] The name V_{KA} center is consistent with the name F_A center used to designate an F center associated with an alkali impurity.

[9] C. E. Bailey, Phys. Rev. 136, 1311 (1964).

DENSITY OF STATES IN NICKEL*

A. J. Blodgett, Jr.,† and W. E. Spicer

Stanford Electronics Laboratories, Stanford University, Stanford, California

(Received 14 April 1965)

In order to understand ferromagnetism in a metal such as nickel, the experience of the past three decades has clearly shown the necessity of determining the electronic quantum states in these materials. In recent years, a number of calculations of the energy band structure of Ni have been made.[1-3] In general, these calculations have been restricted to paramagnetic Ni and have yielded results which suggest that the band structure of Cu[3-5] and that of Ni could be related via the rigid-band model. Several workers have used these calculations and the results obtained from Fermi surface measurements of Cu and Ni to make estimates of the positions and nature of the bands of ferromagnetic Ni.[6,7]

However, the lack of experimental data away from the Fermi surface has made it very difficult to check the validity of the approximations used in the various theoretical models. It is the purpose of this Letter to report an experimental determination of the density of states in Ni over an energy range of 17 eV made by means of photoemission studies. These results are discussed in terms of the density of states in Cu and the various theoretical models.

The use of photoemission to obtain information about band structure has been demonstrated recently by work on various semiconductors[8-11] and metals.[12,13] Vacuum phototubes provided with LiF windows having a high-energy cutoff at 11.6 eV were used. A McPherson monochromator was used for measurements in the vacuum ultraviolet. The other experimental techniques used in the present work have been discussed previously.[14] An attempt to lower the work function of Ni by placing approximately a monolayer of Cs on the surface resulted in the formation of a Ni-Cs alloy; for this reason, the results reported here are for Ni samples without Cs. Since experimental measurements indicated that more than 99% of the surface area had a work function of 5.0 eV, this value has been used in the analysis here.

Energy distributions have been obtained for photon energies from 6.0 to 11.8 eV. Although it is not possible to present all of these data