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ELECTRON NUCLEAR DOUBLE RESONANCE STUDY OF LITHIUM *A* CENTERS IN KCl†

Robert Lee Mieher*
II. Physikalischen Institut der Technischen Hochschule, Stuttgart, Germany

(Received April 2, 1962)

Optical studies[1-3] on KCl have shown a relation between the optical absorption band at 589 mμ, the *A* band, and the sodium impurity content of the crystal. The *A* centers are present after short illumination times of the *F* centers in a freshly quenched crystal. Studies with polarized light have shown that the *A* centers can be polarized in a [100] direction and have a second optical absorption band under the *F* band. It has been proposed[1-3] that the *A* center is an *F* center associated with a Na ion in one of the six nearest neighbor positions. This Letter reports an optical study of a similar center in which the *F* center is associated with a lithium[3] impurity and an electron nuclear double resonance (ENDOR) study that verifies the general *A*-center model of an *F* center associated with an alkali impurity.

Figure 1 shows the optical absorption bands that result when a KCl crystal is grown with 1% LiCl in the melt and then additively colored to a concentration of 3×10^{17} *F* centers/cc. Curve 1 of Fig. 1(a) is the *F*-center absorption band that is present after the crystal is quenched from 650°C to room temperature and then measured at -180°C (all measurements were made at liquid O_2 temperature). Curve 2 of Fig. 1(a) is obtained after five minutes exposure at room temperature to green light centered at 546 mμ. The effects of polarizing the *A* centers with 546-mμ light polarized along a [100] direction is shown in Fig. 1(b). Curve 1 is obtained with [010] polarized measuring light and curve 2 with [100] light.

If the axis of the *A* center is taken to be the line from the vacancy to the impurity, then the A_2 band is excited by light with electric vector perpendicular to the axis of the center and the A_1 band is excited by light with electric vector parallel to the axis (see reference 1 for a general discussion). Table I compares the peak positions of the optical absorption bands in KCl containing Na to those in KCl containing Li.

The results of an ENDOR study of the lithium *A* center are shown in Fig. 2. The meaning of the notation above the ENDOR line is as follows: The +, - superscripts indicate the state of the electron, $m_S=\pm\frac{1}{2}$; the $\parallel$, $\perp$ subscripts indicate the angle between the magnetic field and a line from the vacancy to a given nucleus; the K_α nucleus is the single potassium opposite the lithium, i.e., on the axis of the center, and the K_β nuclei are the four potassiums located in the plane perpendicular to the axis of the *A* center.

The ENDOR spectrum of the nearest neighbor potassium nuclei of the *F* center in a quenched crystal is shown in Fig. 2(a). After an optical treatment similar to that used to produce curve 2 of Fig. 1(a), the ENDOR spectrum appears as given in Fig. 2(b). One interesting feature is the $K_{\alpha\parallel}^-$ quadrupole triplet which consists of three sharp lines. They are about one-half as high as the $K_{\beta\parallel}^-$ lines although there are only one-fourth as many K_α nuclei as K_β nuclei. The explanation is that the K_α nucleus is opposite the Li and, therefore, has no equivalent nucleus to produce the second order hyperfine interaction[4-6] that gives the additional fine structure to the $K_{\beta\parallel}^-$ quadrupole triplet. This explanation is verified in Figs. 2(c) and 2(d). In Fig. 2(c) the *A* centers have been polarized with their axes parallel to the magnetic field and there are strong $K_{\alpha\parallel}^-$ and $Li_\parallel^-$ lines present with very weak $K_{\beta\parallel}^-$ and $Li_\perp^-$ lines. In Fig. 2(d) the crystal has been rotated 90° and the centers are then perpendicular to the field. The relative intensities are just reversed. [The state of the electron, $m_S = -\frac{1}{2}$, for the Li ENDOR lines was determined by measuring the shifts in the ENDOR frequencies when the magnetic field was set to the high- and low-field sides of the electron spin resonance line. The Li^+ lines were not observed because they occur in a low-frequency region where there are many ENDOR lines of the chlorine nuclei.]

If the hyperfine interaction of a given nucleus is axially symmetric (this is not necessarily true for all of the nuclei but will suffice for the present discussion), then to first order in the hyperfine constants the ENDOR frequencies are given by[7,8]

$$h\nu = \pm g_1\beta H_0 + \tfrac{1}{2}[a + b(3\cos^2\alpha - 1)] + Q'(3\cos^2\alpha - 1)(m - \tfrac{1}{2}).$$

The first term represents the interaction of the nucleus with the applied field H_0. The "a" term is a measure of the electron spin density at the nucleus, i.e., the isotropic Fermi contact interaction, the "b" term is the anisotropic dipole-

Table I. Absorption peaks of Na *A* center and Li *A* center in KCl at -180°C.

	F (mμ)	A_2 (mμ)	A_1 (mμ)
KCl-Na[a]	540	528	589
KCl-Li	540	553	629

[a] Taken from reference 1.

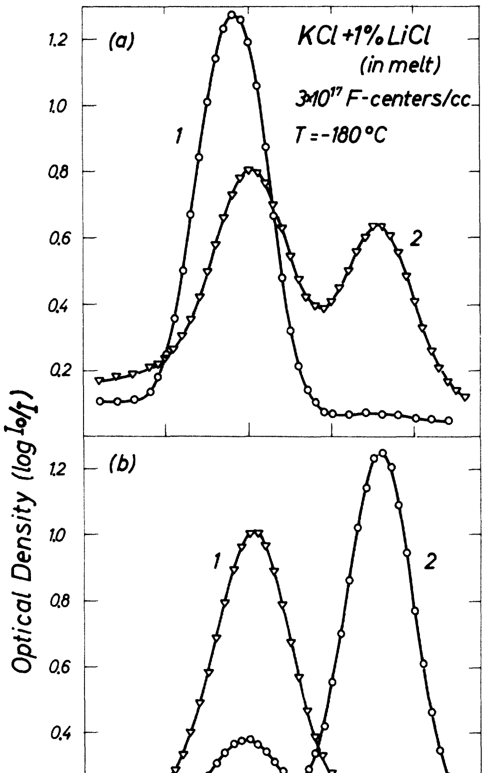

FIG. 1. Optical absorption bands in additively colored, lithium-doped KCl at -180°C. (a) Curve 1 is for *F* centers in crystal after quench from 650°C to room temperature. Curve 2 is for *A* centers in crystal after five minutes irradiation by 546-mμ light (~10^{17} photons/sec-cm^2) at room temperature. (b) Curve 1 shows the absorption of [010] polarized light after polarizing *A* centers at -180°C with [100] polarized 546-mμ light. Curve 2 shows the absorption of [100] polarized light. (The small peak at 550 mμ is caused by some *F* centers and less than 100% alignment of the *A* centers.)

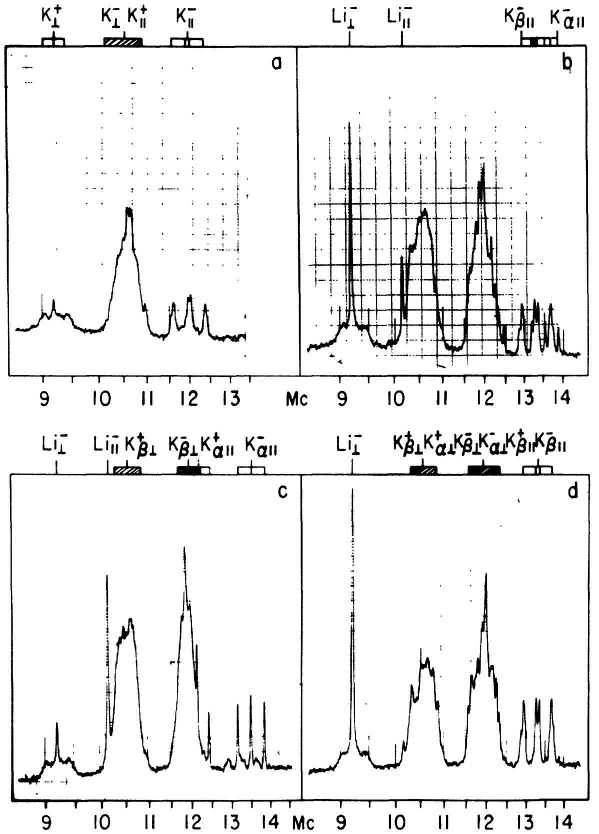

FIG. 2. ENDOR lines of nearest neighbors of *F* centers and *A* centers in lithium-doped KCl at -180°C with H_0 parallel to [100]. (a) *F* centers in crystal after quench from 650°C to room temperature. (b) *A* centers in crystal after five minutes irradiation by 546-mμ light at room temperature. (c) *A* centers polarized parallel to H_0. (d) *A* centers polarized perpendicular to H_0.

Table II. Nearest neighbor hyperfine constants of F center and A center in KCl.

Center	Nucleus	a (Mc/sec)	b (Mc/sec)
KCl: F center[a]	K	20.77	0.94(5)
KCl, Li: A center	K_α	23.71(5)	0.99
	K_β	24.59	0.92(5)
	Li	8.03	0.63

[a] Taken from reference 6.

dipole interaction between the electron and nucleus, and the angle α is the angle between H_0 and a line from the vacancy to the nucleus. The last term is the quadrupole interaction that gives the potassium triplets in Fig. 2 but, since the quadrupole splittings are about the same for the F center and A center, the quadrupole term is not considered in the discussion to follow.

The hyperfine constants for the lithium A centers are compared to those of the unperturbed F center in Table II. Since the "a" hyperfine constants for the A-center potassiums are about 15-20% higher than for the F center, the A center cannot be described by simply mixing some p function into the ground state of an F center in an undistorted lattice. Using the "amplification factors," which are obtained when the F-center wave function is orthogonalized to the ion-core wave functions, as given by Gourary and Adrian,[8] and assuming that the K_α and Li nuclei are equidistant from the vacancy, the predicted ratio of the a values is $a(\text{Li})/a(K_\alpha) = 0.73$ whereas the experimental ratio is 0.34. This indicates that the lithium has been pushed away from the vacancy. Nevertheless, it may not be valid to assume that the effects on the a values of orthogonalizing the A-center wave function to the ion cores can be correctly accounted for by using the F-center amplification factors. Also, there are appreciable differences between the theoretical and experimental a values for F centers. A more reliable indication that the Li ion has moved away from the vacancy is given by the b value. Since the Li ion has no p electrons, the b value is given by the classical dipole-dipole interaction between the electron and the lithium nucleus.[8] If the electron is taken as a point dipole centered in the vacancy, then the experimental b value gives 3.65 Å for the distance from the Li nucleus to the vacancy center. The distance between ions in a perfect KCl lattice is 3.14 Å; if the Li ion were permitted to move out until it touches the next Cl ion, then the vacancy-lithium distance would be 3.70 Å. Nevertheless, an integration of the dipole-dipole interaction over an assumed wave function changes the results considerably. Table III gives a comparison of the theoretical and experimental b values for the F center in LiF and the Li A center in KCl. The A-center calculations assume an undistorted type III Gourary and Adrian F-center wave function. The table indicates that detailed A-center wave-function calculations including exchange would also show that the Li ion is displaced, but perhaps not as far as indicated by the simple point dipole-dipole calculation. Further consideration of the hyperfine constants requires detailed wave-function calculations for the A center.

The author wishes to thank Professor H. Pick for his interest in this research and for the hospitality of the II. Physikalischen Institut. Special acknowledgments are also due Dr. F. Lüty, Dr. H. Seidel, and Dr. H. Wolf who were very generous with their advice and equipment.

Table III. Experimental and theoretical lithium b values.

	Vacancy-nuclear distance (Å)	b (Mc/sec) Point dipoles	b (Mc/sec) Type III	b (Mc/sec) Exchange	b (Mc/sec) Exp.
LiF[a]	2.01	3.79	2.0	2.8	3.2
KCl-Li	3.14	0.99	0.62	...	0.63
KCl-Li	3.70	0.60	0.50	...	0.63

[a] Theoretical values from reference 8. Experimental value from reference 5.

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†This research was supported by the Deutschen Forschungsgemeinschaft.

*Present address: Department of Physics, Columbia University, New York, New York.

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SPIN TRANSITIONS INDUCED BY EXTERNAL rf ELECTRIC FIELD IN GaAs†

E. Brun,* R. Hann, W. Pierce, and W. H. Tanttila
Physics Department, University of Colorado, Boulder, Colorado

(Received April 5, 1962)

Bloembergen and others[1] have shown that upon application of a dc electric field on certain crystals containing nuclei with electric quadrupole moments, one can cause a shift of the nuclear resonance frequency. Further, Bloembergen[2] suggested that transitions between the spin levels of a nucleus in such crystals might be induced by application of electric rf fields at the proper frequency. Ludwig and Ham[3] have recently observed an analogous effect in electron resonance experiments.

We investigated the resonances of Ga^{69}, Ga^{71}, and As^{75} in GaAs. The experiments were performed at liquid nitrogen temperature to minimize the competition of the thermally induced spin transitions. A GaAs single crystal of high resistivity but unknown orientation was placed between two copper plates and the assembly was placed in the coil of a standard single-coil, pulsed induction system. The free-induction decay following a magnetic 90° pulse was observed at 6.77 Mc/sec. An rf generator tuned to 13.54 Mc/sec was connected to the copper plates in order to induce $\Delta m = \pm 2$ transitions. The static magnetic field in which the resonances were observed, the magnetic rf field, and the electric rf field were mutually perpendicular. A decrease of the free-induction signal of all three isotopes was observed for 90° pulses immediately following an appropriate electric excitation of the copper plates. A typical result is shown in Fig. 1. The saturation of the resonances as a function of the applied rf voltage is given in Fig. 2.

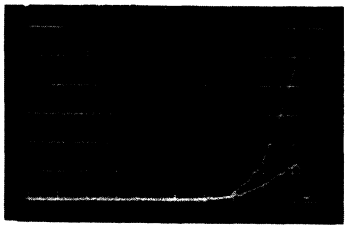

FIG. 1. Typical free-induction decays of Ga^{69}, with and without rf electric field. Horizontal: 100 μsec/div. Vertical: 5 V/div.

Since the linewidths of all three resonances are the same, the amplitude M_z of the free-induction decay is simply[4]

$$M_z = M_0/(1 + kW_1T_1), \tag{1}$$

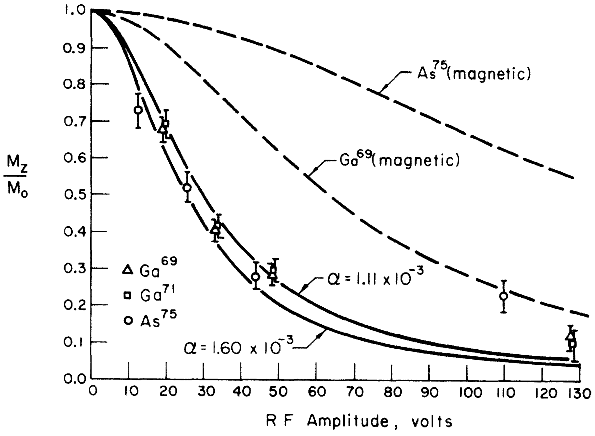

FIG. 2. The experimental points are measured values of the ratios of the amplitudes of the free-induction signals with and without the saturating electric field on. The curves are graphs of the function $1/(1+\alpha V^2)$, where V is the amplitude of the applied rf saturating voltage, and α is chosen for the lower curves to give the best fits to the Ga^{71} and the As^{75} points. The upper, dashed, curves are calculated for Ga^{69} and As^{75}, relative to the best-fit curve for Ga^{71}, assuming a purely magnetic interaction.