PHYSICAL REVIEW VOLUME 91, NUMBER 5 SEPTEMBER 1, 1953

Electronic Structure of *F* Centers: Hyperfine Interactions in Electron Spin Resonance

A. F. Kip, C. Kittel, R. A. Levy, and A. M. Portis
Department of Physics, University of California, Berkeley, California

(Received May 18, 1953)

It is shown that the observed width of the microwave electron spin resonance absorption lines associated with *F* centers in KCl, NaCl, and KBr crystals can be attributed to hyperfine interactions between the *F*-center electron and the nuclear magnetic moments of the ions adjacent to the *F* center. The width arises from the distribution of nuclear moment components. Theoretical calculations of the width are in good agreement with observation provided that the *F*-center wave function is treated as a linear combination of atomic orbitals; wave functions calculated on continuum models are shown to be unsatisfactory. The theory is confirmed by a comparison of observations on *F* centers in crystals of $K^{39}Cl$ and $K^{41}Cl$. If the width is attributed to interactions with the nearest sets of K and Cl ions, the experiments lead directly to quantitative values of the electronic charge density at the K and Cl nuclei: one finds $|\Psi(K)|^2 = 0.70\times 10^{24}$ cm^{-3} and $|\Psi(Cl)|^2 = 0.12\times 10^{24}$ cm^{-3}.

I. INTRODUCTION

In this paper we show that the shape and width of microwave spin resonance absorption lines associated with *F* centers in alkali halide crystals are caused by hyperfine interactions and find a natural explanation on a molecular orbital model of an *F* center.[1] The line width is attributed to the hyperfine interactions between the *F*-center electron and the nuclear magnetic moments of the ions adjacent to the *F* center. This explanation is supported, as shown below, both by theoretical calculations and by a comparison of observations on *F* centers in crystals of $K^{39}Cl$ and in $K^{41}Cl$. The molecular orbital model[2] describes an *F* center, which is an electron attached to a halogen ion vacancy (Fig. 1), by a linear combination of atomic orbitals (LCAO), each representing the extra electron in an atomic state on an atom in the cluster bounding the vacancy. The electron will interact through the *s* components of the atomic orbitals with the nuclear spins of the cluster of alkali atoms. We shall see below that the envelope of the intensity distribution of the hyperfine components of the spin resonance line is approximately Gaussian, and we shall calculate the half-width of the distribution.

Our interest in the *F*-center problem arose from the observation by Hutchison and Noble[3] that the width of the electron spin resonance absorption line in a KCl crystal colored by the addition of the order of 10^{18} excess K atoms per cm^3 was 49 oersteds between points of maximum slope in absorption. The line shape was reported to be Gaussian, so that the full width at half-maximum absorption is presumably about 56 oersteds. The observed shape and width are in marked disagreement with the theory of dipolar interactions. The theoretical magnetic dipolar width[4] for the actual *F* center concentration, assuming *F* centers distributed at random in the crystal lattice, is of the order of 0.1 oersted, and the theoretical line shape is Lorentzian.

Prompted by the above discrepancy, we investigated experimentally the spin resonance line associated with *F* centers in KCl crystals colored additively at various concentrations and quenching rates and also colored at room temperature by 2.5-Mev electron bombardment and by 250-kev x-ray irradiation. Microwave measurements were made at room and liquid nitrogen temperatures. In all of our measurements on KCl the line shape was approximately Gaussian, and the width was in very close agreement with the value observed by Hutchison and Noble. Our observations suggest then that the width of the resonance line is not caused by interactions between the *F* centers, but rather by the interactions of an *F*-center electron with its immediate environment in the crystal. The dominant interaction of this type is the hyperfine interaction between the *F*-center electron and the nuclear magnetic moments of the ions adjacent to the *F* center.

Most of the theoretical calculations of wave functions of *F* centers have treated the crystal as a homogeneous dielectric continuum,[5] with the electron moving in a

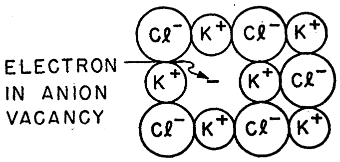

FIG. 1. *F* center in KCl. The ionic radii are drawn approximately to scale, but the distortion of the lattice near the *F* center is not included.

---

[1] A preliminary account of this work was given by C. Kittel, Bull. Am. Phys. Soc. **28**, No. 2, 21 (1953).

[2] T. Muto, Progr. Theoret. Phys. **4**, 243 (1949); T. Inui and Y. Uemura, Progr. Theoret. Phys. **5**, 252, 395 (1950); see also a related calculation by S. R. Tibbs, Trans. Faraday Soc. **35**, 1471 (1939).

[3] C. A. Hutchison, Jr. and G. A. Noble, Phys. Rev. **87**, 1125 (1952); earlier resonance experiments on *F*-centers are reported by C. A. Hutchison, Jr., Phys. Rev. **75**, 1769 (1949); E. E. Schneider and T. S. England, Physica **17**, 221 (1951); M. Tinkham and A. F. Kip, Phys. Rev. **83**, 657 (1951).

[4] For N electrons/cm^3 distributed at random on a simple cubic lattice, $\Delta H \approx N\times 10^{-19}$ oersteds, provided that the fractional population is less than 0.01; this estimate uses the theory developed by C. Kittel and E. Abrahams, Phys. Rev. **90**, 238 (1953). Hutchison and Noble calculate values using an incorrect theory of the line width for random population.

[5] Typical of calculations of this character are those of S. R. Tibbs, Trans. Faraday Soc. **35**, 1471 (1939); J. H. Simpson, Proc. Roy. Soc. (London) **A197**, 269 (1949); L. Pincherle, Proc. Phys. Soc. (London) **A64**, 648 (1951); J. A. Krumhansl and N. Schwartz, Phys. Rev. **89**, 1154 (1953); C. I. Pekar, J. Exptl. Theoret. Phys. **16**, 335 (1946); **17**, 868 (1947); **19**, 746 (1949); **20**, 510 (1950).

central field. Such calculations take no account of the singularities in the potential which occur at the nuclei of the ions adjacent to the *F* center. We should not expect such wave functions to give correct estimates of the hyperfine interactions, and in fact we shall find that the calculated line width using Simpson's wave functions for NaCl is only of the order of several oersteds. Further, it was shown earlier by Kahn and Kittel[6] that the central field model is unable to account for the observed g value of the *F*-center resonance, and they proposed instead a molecular orbital model which gives correctly the order of magnitude of the observed Δg. It will be seen below that their model gives quite satisfactory values for the line width in KCl.

II. ELEMENTARY THEORY FOR KCl

We represent the *F* center, following Kahn and Kittel, by the molecular orbital

$$\Psi=(1/6)^{\frac{1}{2}}\sum_{i=1}^{6}\psi_i; \tag{1}$$

here ψ_i is the wave function of the valence electron when on the ith of the six K^+ ions bounding the anion vacancy. Taking the ψ_i as normalized, then Ψ will be normalized apart from overlap integrals which we neglect for the present; the results of Secs. III and IV below do not involve this assumption. On a free potassium atom ψ_i would be a $4s$ function, but in the crystal the state becomes electrically polarized[6] by the unsymmetrical crystal field which exists near the vacancy. We denote the fractional effective s character[7] of ψ_i by ξ, in the sense that in the crystal the value of $|\psi_i(0)|^2$ at a nucleus is equal to ξ times the free atom value of $|\psi_{4s}(0)|^2$; here $\xi\leqq 1$. We have then for the part of the Hamiltonian describing the hyperfine interaction with the alkali atom nuclei of spin I:

$$\mathcal{H}'=\tfrac{1}{6}\xi A\mathbf{S}\cdot\sum\mathbf{I}_i, \tag{2}$$

where $A\mathbf{S}\cdot\mathbf{I}$ is the interaction in the free atom. For K^{39}, the most abundant (93 percent) isotope of potassium, the coupling constant A has the value 0.0077 cm^{-1}, according to Fox and Rabi.[8]

When the Zeeman energy of the system is large in comparison with the hyperfine coupling we may treat the latter as a small perturbation on the Zeeman energy levels. In the representation in which M_s, $m_I(1)$, $m_I(2)$, $\cdots$, $m_I(6)$ are diagonal, the diagonal matrix elements of $\mathcal{H}'$ are

$$(M_sm_I(1)\cdots m_I(6)|\mathcal{H}'|M_sm_I(1)\cdots m_I(6)) =\tfrac{1}{6}\xi^2AM_sM_I. \tag{3}$$

The interaction of an rf field in the x direction with the system is described by the term

$$\mathcal{H}_{\text{rf}}=-(g\mu_BS_x+g_n\mu_n\sum I_{xi})H_x, \tag{4}$$

where g_n, μ_n refer to the nuclei. As $g_n\mu_n/g\mu_B$ is of the order of 10^{-3}, the transitions induced by H_x in which the nuclear spins change orientation are much weaker than those in which the electron spins change orientation; the nuclear transitions are neglected. We are thus led to the approximate selection rule $\Delta M_s=\pm1$; $\Delta M_I=0$. The absorption frequencies are given by

$$\hbar\omega=g\mu_BH_0+\tfrac{1}{6}\xi AM_I. \tag{5}$$

For six nuclei each of spin $\frac{3}{2}$ the maximum value of $\frac{1}{6}AM_I$ is $\frac{3}{2}A$, or 0.0115 cm^{-1}. This is equivalent (for $g=2$) to 123 oersteds: thus the effect of the hyperfine interaction is to spread out the transition over a region 123ξ oersteds to either side of the central Zeeman frequency.

The shape of the resulting line will be determined by the distribution of M_I values. As each nucleus has four possible values of m_I, there will be $4^6=4096$ arrangements of the six spins. These are distributed as follows among the several M_I values:

M_I	9	8	7	6	5	4	3	2	1	0
No. of arrangements	1	6	21	56	120	216	336	456	546	580

The negative values of M_I are distributed in the same fashion as the positive values. A Gaussian curve of the same integrated line strength and adjusted to fit at $M_I=0$ gives an excellent fit all the way along the envelope, the deviations being less than 2 percent of the central value. The envelope of the hyperfine lines therefore may be considered to be Gaussian to a good approximation, in agreement with the experimental result.

The width of the envelope at half-maximum is $1.12\xi A$, or, for potassium, 92ξ oersteds. The observed width of the *F*-center line is 54 ± 2 oersteds, suggesting that $\xi\cong0.6$, which means that the atomic orbitals have 0.6 s character. Values of ξ are expected to be of the order of one-half, from considerations of the electrostatic polarization of the potassium atom towards the interior of the negative ion vacancy. We note that a mixture of s and p_z orbitals has its maximum dipole moment when the coefficients of the s and p_z parts are equal. Values of this order are also required[6] to account for the g shift. One should expect that higher angular momenta will also be present and that the electron may penetrate beyond the first shell of K ions. For these various reasons we may consider the measure 0.6 of

---

[6] A. H. Kahn and C. Kittel, Phys. Rev. **89**, 315 (1953).

[7] The components of higher orbital angular momenta mixed in this way into the ground state are almost completely quenched, and the states contribute to the hyperfine interaction only through the electron spin. The spin contribution in the potassium $4p$ level is less than 0.1 of the orbital contribution, and further, the total hyperfine splitting in p states in potassium and lighter alkali atoms is only about 0.1 of the corresponding s-state splitting. Thus the quenched p state hyperfine interaction may be in potassium of the order of only 0.01 of the s state interaction. We therefore neglect here the hyperfine splitting from the $4p$ and higher states. In Cs and Rb it may be worth while to include the p state effects.

[8] M. Fox and I. Rabi, Phys. Rev. **48**, 746 (1935); for a tabulation for alkali atoms, see J. B. M. Kellogg and S. Millman, Revs. Modern Phys. **18**, 323 (1946).

the s character of the atomic orbitals to be quite reasonable and consistent with other evidence.

We now compare the value of the effective coupling constant deduced from the observed line width with estimates made using the conventional theoretical model of the F-center ground state as a 1s state in a central field. Simpson[9] has calculated on this basis the wave function in NaCl, and we may safely consider that the wave function in KCl would be closely similar. Taking $|\Psi|^2$ at the center of a sodium ion from this wave function, the coupling constant works out as 1.4×10^{-5} cm^{-1} between the F-center electron and an individual K nucleus. The observed line width, however, points to a coupling constant,

$$\tfrac{1}{6}\xi A=77\times 10^{-5}\ \mathrm{cm}^{-1},$$

about 50 times larger. We therefore conclude that the central potential does not give an adequate representation of the actual wave function, whereas the molecular orbital model discussed above leads quite naturally to interactions of the correct order of magnitude.

III. GENERAL THEORY

It is of interest to derive general expressions for the mean-square and mean-fourth frequency deviations of electron spin resonance lines in the presence of hyperfine interactions. The generalization of the above results consist in the application of the method of sums to interactions with a mixture of atoms with various nuclear moments and nuclear spins. The generalization will enable us to consider conveniently the effect on the line width of interactions with the anions beyond the first shell of cations bounding the vacancy. The first anion shell in KCl has $4^{12}\cong 17\times 10^6$ spin arrangements, so that it is impractical to enumerate the arrangements individually.

We have the perturbation Hamiltonian,

$$\mathcal{H}=\sum_i a_i \mathbf{S}\cdot\mathbf{I}_i, \tag{6}$$

where[10]

$$a_i=\frac{-16\pi}{3}\frac{\mu_B\mu_i}{I_i}|\Psi(i)|^2. \tag{7}$$

Here μ_i is the magnetic moment of nucleus i; I_i is the spin of nucleus i; and $\Psi(i)$ is the value of the normalized electron wave function at the position of nucleus i. The absorption frequencies are

$$\hbar\omega=g_e\mu_B H_0+\sum a_i I_i^z, \tag{8}$$

according to Eq. (5). Thus the mean-square deviation from the central frequency is

$$\langle(\hbar\Delta\omega)^2\rangle_{\mathrm{Av}}=\langle(g_e\mu_B\Delta H)^2\rangle_{\mathrm{Av}}=\langle\textstyle\sum_i(a_iI_i^z)^2\rangle_{\mathrm{Av}}, \tag{9}$$

or

$$\langle(\Delta H)^2\rangle_{\mathrm{Av}}=\langle\textstyle\sum_i(h_iI_i^z)^2\rangle_{\mathrm{Av}}=\textstyle\sum_i h_i^2\langle m_i^2\rangle_{\mathrm{Av}}, \tag{10}$$

where

$$h_i=(8\pi\mu_i/3I_i)|\Psi(i)|^2, \tag{11}$$

and m_i is the value of I_i^z. Similarly,

$$\langle(\Delta H)^4\rangle_{\mathrm{Av}}=\sum h_i^4\langle m_i^4\rangle_{\mathrm{Av}}. \tag{12}$$

Now

$$\langle m_i^2\rangle_{\mathrm{Av}}=\tfrac{1}{3}I_i(I_i+1),$$

so that

$$\langle(\Delta H)^2\rangle_{\mathrm{Av}}=\tfrac{1}{3}\sum h_i^2 I_i(I_i+1)$$
$$=\frac{64\pi^2}{27}\sum\mu_i^2\frac{I_i+1}{I_i}|\Psi(i)|^4. \tag{13}$$

This is the most useful result of the theory.

We note that

$$\langle m_i^4\rangle=\tfrac{1}{5}I_i(I_i+1)[I_i(I_i+1)-\tfrac{1}{3}], \tag{14}$$

so that if all the nuclei are similar and the h_i are equal,

$$\frac{\langle m_i^4\rangle^{\frac{1}{4}}}{\langle m_i^2\rangle^{\frac{1}{2}}}=\left\{\frac{9}{5}\frac{[I_i(I_i+1)-\frac{1}{3}]}{I_i(I_i+1)}\right\}^{\frac{1}{4}}. \tag{15}$$

For a Gaussian line this ratio should be equal to $(3)^{\frac{1}{4}}=1.32$. For spin $\frac{3}{2}$, as in K^{39} and K^{41}, it is actually equal to 1.13. The discrepancy is not significant as the actual line has a finite cutoff, while the Gaussian has not. The explicit determination of the envelope for a special case in Sec. II gave a shape close to Gaussian.

IV. ANALYSIS OF RESULTS WITH K^{39}Cl AND K^{41}Cl

In Sec. II above we saw that hyperfine interactions appear to account for the width of the spin resonance line associated with F centers in KCl. A critical test of this hypothesis is provided by the comparison of line widths in natural KCl with K^{41}Cl. The isotope abundances in natural potassium are: K^{39}, 93.08 percent; K^{40}, 0.012 percent; K^{41}, 6.91 percent. The ratio of the magnetic moments $\mu(41)/\mu(39)$ is 0.550, or $\mu(41)/\langle\mu(\mathrm{natural})\rangle_{\mathrm{rms}}=0.563$, so that if the hyperfine interactions are principally with the potassium ions bordering the anion vacancy, the resonance line should be appreciably sharper for F centers in K^{41}Cl than in natural KCl. It would be naive, however, to expect that the line width would be exactly in the ratio of the moments, as the ground-state energy calculations by Inui and Uemura[2] suggest that the neighboring Cl$^-$ ions do bear a part of the wave function.

We obtained through the courtesy of the Stable Isotopes Division of the U. S. Atomic Energy Commission the loan of 1.8 grams of powdered K^{41}Cl, in which the K^{41} had been concentrated electromagnetically at Oak Ridge. The potassium isotope abundances reported for the specimen are: K^{39}, 0.789 percent; K^{40}, 0.002 percent; K^{41}, 99.21 percent. We fused the powder in a procelain crucible and then colored the resulting specimen by x-ray irradiation at room temperature with 250-kev x-rays.

---

[9] J. H. Simpson, Proc. Roy. Soc. (London) **A197**, 269 (1949).

[10] E. Fermi and E. Segrè, Z. Physik **82**, 729 (1933).

TABLE I. Data on nuclear magnetic moments relevant to the present paper.

Isotope	Natural abundance (percent)	Spin	Magnetic moment (nuclear magnetons)	Hyperfine coupling constant, ground state of free atom (cm^{-1})
Na^{23}	100.	3/2	2.217	0.0296
K^{39}	93.08	3/2	0.391	0.00770
K^{41}	6.91	3/2	0.215	0.00424
$\langle\mathrm{K(natural)}\rangle_{\mathrm{rms}}$	···	3/2	(0.382)	(0.00752)
Rb^{87}	27.85	3/2	2.750	0.114
Cs^{133}	100.	7/2	2.577	0.0767
Cl^{35}	75.4	3/2	0.822	···
Cl^{37}	24.6	3/2	0.684	···
$\langle\mathrm{Cl(natural)}\rangle_{\mathrm{rms}}$	···	3/2	(0.790)	···
Br^{79}	50.52	3/2	2.11	···
Br^{81}	49.48	3/2	2.27	···
$\langle\mathrm{Br(natural)}\rangle_{\mathrm{rms}}$	···	3/2	(2.189)	···

Microwave spin resonance measurements on the colored $\mathrm{K}^{41}\mathrm{Cl}$ specimen gave a line width of 36±2 oersteds, as compared with 54±2 oersteds for the colored natural KCl specimen. If only the first set of K^+ ions bordering the vacancy shared in the *F*-center wave function we should expect a width of 31 oersteds in the $\mathrm{K}^{41}\mathrm{Cl}$. The extent of the agreement is a convincing indication that the line width is actually caused by hyperfine interactions, but the small discrepancy between the observed and calculated values suggests that the Cl^- ions also share in the *F*-center wave function.

We shall now analyze the data for potassium chloride on the following simplifying assumptions:

(1) The *F*-center wave function overlaps only the six nearest neighbor K ions and the twelve next nearest neighbor Cl ions.

(2) The *F*-center wave function at the nuclei has the same density in $\mathrm{K}^{39}\mathrm{Cl}$ and in $\mathrm{K}^{41}\mathrm{Cl}$.

(3) Isotopic mixtures are treated using root-mean-square values of the magnetic moments (Table I); this procedure is rigorously correct.

(4) The resonance line shape is treated as if it were Gaussian, so that the width at half-maximum absorption is taken as 2.35 times the root-mean-square width.

(5) Hyperfine interaction is the only significant source of line broadening.

We have from Eq. (13), the ratio of the K moments, and the observed widths:

$$\begin{aligned} 530 &= 7.5h^2(\mathrm{K})+15h^2(\mathrm{Cl}); \\ 235 &= (7.5)(0.317)h^2(\mathrm{K})+15h^2(\mathrm{Cl}). \end{aligned} \tag{16}$$

Here K denotes natural potassium. Then

$$h(\mathrm{K})=7.56\ \text{oersteds};\quad h(\mathrm{Cl})=2.57\ \text{oersteds}. \tag{17}$$

Using Eqs. (11) and (17), we find for the charge densities at the nuclei:

$$\begin{aligned} |\Psi(\mathrm{K})|^2 &= 0.70\times10^{24}\ \mathrm{cm}^{-3}; \\ |\Psi(\mathrm{Cl})|^2 &= 0.12\times10^{24}\ \mathrm{cm}^{-3}. \end{aligned} \tag{18}$$

These are to be considered as approximate experimental values of the electron densities at the nuclei of the nearest K and Cl ions bordering the *F* center. It is seen that the Cl ions play a much smaller role than do the K ions. By contrast with the above values, continuum wave functions give values of the order of $0.02\times10^{24}\ \mathrm{cm}^{-3}$ for $|\Psi(\mathrm{K})|^2$. It would seem reasonable to judge the accuracy of future wave function calculations by the extent of the agreement of the calculated $|\Psi|^2$ values with the values given in Eq. (18).

We can calculate $|\psi(0)|^2$ for the 4*s* state of a free potassium atom by use of Eq. (7) and the experimental coupling constant obtained from atomic beam results.[8] We find $|\psi(0)|^2=7.5\times10^{24}\ \mathrm{cm}^{-3}$. This may be compared with $6|\Psi(\mathrm{K})|^2=4.2\times10^{24}\ \mathrm{cm}^{-3}$ from Eq. (18); the comparison means, in general agreement with the earlier estimate, that the *F*-center wave function on the nearest *K* ions has 56 percent of the *s* character that one would have with a linear combination of 4*s* atomic orbitals on the potassium atoms only. This high percentage tells us that the wave function must be strongly localized in the immediate vicinity of the anion vacancy. If the wave function covered a large number of K atoms equally, we note that the line width would diminish proportional to $(1/N)^{\frac{1}{2}}$, where *N* is the number of atoms involved. It seems likely that, by analogy with metallic potassium, the overlap effects in the normalization integral are considerable and act to increase the charge density at the nuclei. The nearest neighbor distance between K ions is roughly the same in the metal as in KCl.

V. *F* CENTERS IN NaCl AND KBr

We have now under way a substantial program to investigate *F*, *V*, and other centers in the alkali halides, alkaline earth salts, and other crystals, including situations (such as with zero nuclear spin) where the hyperfine interactions may be small enough to give a sharp resonance line and situations (as in cesium and rubidium salts) where the cation hyperfine interaction may be large enough to enable individual hyperfine components to be resolved, provided the nearest neighbor shell of cations does not contribute significantly to the interaction. The only other *F*-center measurements we are able to report at present are for NaCl, where the width is 162 oersteds, and for KBr, where the width is 146 oersteds. The NaCl and KBr crystals were measured at the temperature of liquid nitrogen. The NaCl was colored by bombardment with 2.5-Mev electrons from the electron linear accelerator stage of the Berkeley synchrotron.[11] The KBr was colored additively.

We shall now try to understand approximately these two widths, considering first the width in NaCl. We shall suppose for the purpose of the estimate that the contributions of the Cl ions in NaCl to the mean-square

---

[11] We are indebted to Mr. George MacFarland and Mr. Duane Mosier of the University of California Radiation Laboratory for the electron bombardments.

line width is the same as in KCl, and that the contribution of the Na ions is related to that of the K ions by the ratio of the hyperfine coupling constants in the free atom. According to Table I, this ratio is $296/75 = 3.94$. On these assumptions the calculated mean-square width in NaCl is, from Eq. (16),

$$(7.5)(3.94)^2(7.5)^2+(15)(2.7)^2 \cong 6500, \tag{19}$$

which corresponds to a calculated width at half-maximum absorption of 190 oersteds. The observed width in NaCl is 162 oersteds. The agreement is generally satisfactory in view of the sweeping nature of the assumptions on which the estimate is based.

In making an estimate for KBr, we assume that the contribution of the K ions is the same as in KCl. It is assumed further that the contribution of the Br ions is related to that of the Cl ions by the ratio of the coupling constants. The ratio of the coupling constants is estimated in an indirect way from the coupling constants of atomic Rb and K, these atoms being isoelectronic with the Br^{2-} and Cl^{2-} ions. We consider Rb^{87}, as it has a spin of $\frac{3}{2}$. All the other nuclei involved have also spins of $\frac{3}{2}$. The relevant data are given in Table I. The coupling constant ratio $\mathrm{Rb}^{87}/\mathrm{K}^{39}=14.8$; as we are interested in an estimate of the coupling constant ratio $\langle \mathrm{Br}\rangle_{\mathrm{rms}}/\langle \mathrm{Cl}\rangle_{\mathrm{rms}}$ we must multiply 14.8 by the magnetic moment ratio $\langle \mathrm{Br}\rangle_{\mathrm{rms}}/\mathrm{Rb}^{87}=0.80$ and also by the magnetic moment ratio $\mathrm{K}^{39}/\langle \mathrm{Cl}\rangle_{\mathrm{rms}}=0.50$ In this way we have as a rough estimate the coupling constant ratio $\langle \mathrm{Br}\rangle_{\mathrm{rms}}/\langle \mathrm{Cl}\rangle_{\mathrm{rms}} \approx 5.9$. The mean-square line width on this basis would be, from Eq. (16),

$$7.5(7.5)^2+15(2.7)^2(5.9)^2 \approx 4200 \tag{20}$$

which corresponds to a calculated width at half-maximum absorption of about 153 oersteds. The observed width in KBr is 146 oersteds.

VI. EXPERIMENTAL

With the exception of the $\mathrm{K}^{41}\mathrm{Cl}$, measurements were made on single crystals obtained from the Harshaw Chemical Company. For KCl and KBr, measurements were also made on polycrystalline pellets fused from material obtained from the J. T. Baker Chemical Company. These pellets contained less than 0.0001 percent of paramagnetic impurities. In the absence of coloration of the samples no resonance absorption was observed. By varying the irradiation time for the electron and x-ray bombarded samples, and by varying the temperature of the furnace and quenching rate for the additively colored specimens, it was possible to obtain measurements over a range of *F*-center concentrations from 5×10^{16} to $10^{18}/\mathrm{cm}^3$, as determined spectroscopically from the strength of the optical absorption in the *F* band.

The samples were mounted on blocks cut from Styrofoam and placed at the center (the region of lowest E and highest H field) of a rectangular cavity resonant for the TE_{102} mode at approximately 8950 Mc/sec. The samples were rectangular in shape, nearly filling the cavity cross section. The sample thickness was adjusted to reduce the unloaded Q of the cavity to about $\frac{2}{3}$ of its value in the absence of the sample; the sample volume was generally of the order of 1 cm^3.

A 2K39 reflex Klystron amplitude modulated at 6 kc/sec was employed as the microwave source. The variation in power reflected from the cavity was detected by a specially selected 1N23 crystal placed in one arm of a magic-tee bridge. The 6-kc/sec signal was amplified by a narrow-band low-noise amplifier at a voltage gain of about 10^4. The resonance envelope was detected in a lock-in mixer and presented on the screen of a long persistence cathode-ray oscilloscope, whose horizontal deflection was made to vary linearly with the magnetic field. The field was swept at a rate compatible with a band pass of about 0.1 cps. Field markers obtained from a rotating flux meter bridge were superimposed on the oscilloscope trace. The experimental data were obtained from photographs of the oscilloscope presentation.

For reasons discussed more fully in the following paper, it was found possible to make more accurate measurements on the dispersion envelope than on the absorption. We present in Table II our measurements of g values and of full width between points of maximum dispersion. The dispersion curves were closely Gaussian; we present also for comparison the equivalent (calculated) full width at half-maximum absorption for the corresponding absorption curves. Our results on g value, shape, and width were found to be characteristic only of the particular alkali halide investigated and independent of the concentration of *F* centers, method of preparation, or temperature at which the resonance was observed.

The g values may presumably be interpreted along the lines suggested by Kahn and Kittel[6] for KCl, but we are not able at this time to give a detailed discussion of the differences among the g values of the several salts; this must await the calculation of very good wave functions for the ground and excited states. Configuration interaction might be expected to play a significant part in the g value.

We should emphasize the great importance (to accurate line width determinations) of saturation

TABLE II. Summary of experimental results on *F*-center resonance.

Crystal	g	Observed full width between points of maximum dispersion (oersteds)	Equivalent full width between points of half-maximum absorption (oersteds)
KCl	1.995	61	54
$\mathrm{K}^{41}\mathrm{Cl}$	1.995	40	36
KBr	1.980	162	146
NaCl	1.987	180	162

effects. It is very easily possible to make serious errors through their neglect. The following paper by A. M. Portis discusses the saturation effects in detail.

VII. CONCLUSION

From the experiments and calculations described above it appears that one may with some confidence attribute to hyperfine interactions the width of the electron spin resonance line arising from *F* centers in alkali halide crystals. It appears further than an *F*-center wave function which is a linear combination of polarized atomic orbitals will give a fair quantitative representation of the hyperfine interactions. It is also possible to make reasonable empirical estimates of the line widths on the basis of the results for $K^{39}Cl$ and $K^{41}Cl$, together with the free atom hyperfine coupling constants for the atoms under consideration. Our interpretation of the observed resonance line is also supported in detail by observations by Portis and Kip[12] on the rf saturation behavior of the resonance.

We are glad to acknowledge again our indebtedness to the U. S. Atomic Energy Commission for the provision of the $K^{41}Cl$. We thank the U. S. Naval Radiological Defense Laboratory, San Francisco, for the x-ray irradiations and the University of California Radiation Laboratory for the electron bombardments. The planning of the $K^{41}Cl$ experiment was assisted greatly by the generous advice and encouragement of Professor E. Segrè. We have profitted from discussions with L. W. Alvarez, I. Estermann, W. D. Knight, and F. Seitz. This research was supported in part by the U. S. Office of Naval Research.

---

[12] A. M. Portis and A. F. Kip, Bull. Am. Phys. Soc. **28**, No. 2, 9 (1953); A. M. Portis (following paper), Phys. Rev. **91**, 1071 (1953).

PHYSICAL REVIEW VOLUME 91, NUMBER 5 SEPTEMBER 1, 1953

Electronic Structure of *F* Centers: Saturation of the Electron Spin Resonance

A. M. Portis
Department of Physics, University of California, Berkeley, California

(Received May 18, 1953)

It is shown that the unusual observed saturation behavior of the microwave electron spin resonance associated with *F* centers in KCl, NaCl, and KBr crystals can be accounted for if the overall width is ascribed to interaction between the *F*-center electrons and the nuclear magnetic moments of the ions adjacent to the *F* centers. The measured saturation factor gives for *F* centers in KCl a spin-lattice relaxation time of 2.5×10^{-5} sec at room temperature. The observed saturation behavior in which only the absorption saturates is in marked disagreement with the Kramers-Kronig relations. However it is shown, that the Kramers-Kronig relations are not applicable to saturated systems. Expressions which avoid the use of these relations are presented for saturable systems.

I. INTRODUCTION

It is shown in this paper that the unusual saturation behavior of the microwave spin resonance absorption and dispersion associated with *F* centers in alkali halide crystals can be accounted for if the over-all width is caused by hyperfine interaction.[1] The details of the saturation behavior of a system depend markedly on the nature of the broadening mechanism. If the broadening arises from dipolar interaction between like spins or from interaction with the radiation field, then the thermal equilibrium of the spin system will be preserved during resonance absorption. This will also be true if the line width comes from some mechanism which is external to the spin system but is fluctuating rapidly compared with the time associated with a spin transition. This first case we call the *homogeneous* case. The consequence of homogeneous broadening is that the energy absorbed from the microwave field is distributed to all the spins and thermal equilibrium of the spin system is maintained through resonance. In an effort to understand the observed saturation results, our measurements were first compared with the behavior expected for this kind of broadening. This comparison is shown in Fig. 1. The observed and the theoretical behavior for a simple line of the observed shape were fitted so as to have the same slope at low microwave fields. It can be seen that the simple theory completely fails to account for our saturation results.

In attempting to account for our results we realized that if the line width were to come from variations in the local magnetic fields the physical response of the system would be markedly different. For this second case, which we call the inhomogeneous case, energy will be transferred only to those spins whose local fields satisfy the resonance condition. Further, the processes for spin-spin interaction will be slow as compared with the direct interaction of the spins with the lattice, since in order for spins in different local fields to come to equilibrium, energy will have to be transferred to the lattice. It is useful for this case to think of spin packets

---

[1] A preliminary account of this work was given by A. M. Portis and A. F. Kip, Bull. Am. Phys. Soc. **28**, No. 2, 9 (1953).