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Electron Spin Resonance of the Z_1 Band in KCl with $SrCl_2$†

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The electron spin resonance (ESR) associated with the Z_1 optical absorption in KCl:Sr has been observed in association with the F-center ESR. By an extrapolation procedure, it is found that the Z_1 ESR is characterized by a g value of 1.9952 ± 0.0005 and a derivative peak-to-peak width of 63 ± 1 Oe. A Gaussian shape for the Z_1 ESR is strongly inferred. Preliminary results obtained with F and Z_2 centers present indicate that the Z_2 ESR has a slightly larger g value and a somewhat greater width than the Z_1 ESR. Optical absorption parameters of $h\nu_{\max}=2.068\pm0.005$ eV (599 mμ) and $W=0.290\pm0.005$ eV are found for the Z_1 band at liquid nitrogen temperature.

The ESR results are compared to earlier measurements by Kawamura and Ishiwatari. An attempt is made to interpret the results by comparing Seitz's model of the Z_1 center to the F center. There are tentative indications that Seitz's model may be appropriate, but the calculations are not yet sufficiently refined to establish the model with any degree of certainty. An estimate is made of the rather large hyperfine interaction to be expected for Z_1 centers containing Sr^{87} nuclei.

I. INTRODUCTION

EXPERIMENTAL facts were first reported by Pick[1] who presented a tentative set of models for a sequence of optical-absorption bands (the Z bands) observed in colored KCl crystals containing alkaline earth impurities. More recently, Seitz[2] has summarized the available information on these bands and has proposed a new set of models for the color centers associated with them. (See Fig. 1.) Numerous investigators[3,4] have attempted to correlate the models with the optical bands. There has been no decisive result, although the experimental evidence tends to favor the models of Seitz. The key difficulty which obscures the interpretation of experiments in this field is the presence of the F band in any Z-center investigation.

All of the models of the Z_1 and Z_2 centers have an unpaired electron spin, but the Z_3 center has paired electrons in either case. Thus, both sets of Z_1 and Z_2 center models indicate that paramagnetism should be associated with crystals exhibiting the corresponding optical-absorption bands. The parameters needed to describe the ESR of the Z_1 and Z_2 bands should aid in selecting the correct set of models.

The ESR data taken during the course of this investigation were carefully correlated with optical data. Knowledge of the optical band structure was necessary in order to determine the relative concentrations of F and Z_1 centers and to guard against the presence of other centers that might contribute to the ESR signal.

II. EXPERIMENTAL PROCEDURE

The KCl crystals were grown in air from reagent-grade chemicals by withdrawal from the melt in a Vycor crucible at 0.5 cm/h. The impurity-doped crystals were grown from a melt containing 5×10^{-4} mole fraction of strontium chloride; this would indicate about 10^{-4} as the mole fraction of strontium ion in the doped crystals.[5] The crystals were colored to an F-center density of about 5×10^{-16} per cm^3 either additively with sodium metal vapor in the range between 500 and 600°C or by γ rays from a Co^{60} source. Additively colored crystals were preferred for this investigation since the total color-center concentration did not diminish appreciably during the bleaching processes. Furthermore, additively colored samples did not present the hazard of having any V centers present.

The Z_1 band was developed by bleaching the additively colored, doped crystals with light of wavelength 490 mμ. This is the wavelength, calculated from the data of Camagni and Chiarotti,[3] at which the optical absorption of the F band is maximized with respect to the Z_1 band; hence, the development of bands other than the Z_1 is minimized. Optical absorption curves were determined between 400 and 2000 mμ with a Beckman Model DK Recording Spectrophotometer.

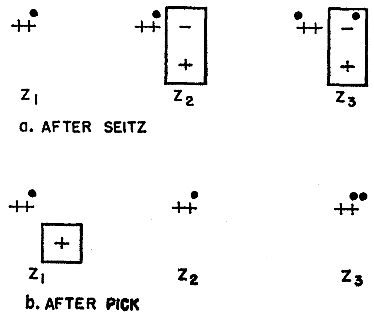

FIG. 1. Proposed Z-center models. The square boxes represent vacancies, ++ represents a substitutional divalent ion, and ● represents a trapped electron.

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[1] H. Pick, Ann. Physik **35**, 73 (1939).

[2] F. Seitz, Phys. Rev. **83**, 134 (1951).

[3] P. Camagni and G. Chiarotti, Nuovo Cimento **11**, 1 (1954).

[4] G. R. Cole and R. J. Friauf, Phys. Rev. **107**, 387 (1957).

[5] H. Kelting and H. Witt, Z. Physik **126**, 617 (1949).

The absorption curves were made at both room temperature and liquid-nitrogen temperature in order to check the optical parameters and to look for the presence of undesired bands.

The ESR experiments were done in the X band at a frequency of about 9400 Mc/sec using a reflection tee bridge and superheterodyne detection. A 2K25 klystron was frequency stabilized using the sample cavity in one of the sidearms of the bridge. The opposite sidearm contained the bridge tuning elements of a variable attenuator and adjustable short. The sample cavity was made of dominant mode rectangular waveguide for TE_{102} operation. The KCl crystal was centered in the cavity with a maximum in high-frequency magnetic-field standing-wave pattern directed approximately along the 100 axis.

The gyromagnetic ratio of the ESR was measured by comparison to DPPH (α, α diphenyl-β-picryl hydrazyl). Since the resonance of DPPH is slightly anisotropic, the use of a single crystal must be avoided, but a polycrystalline sample can easily be prepared from powered material.[6] The g values of the F and Z_1 centers are calculated relative to 2.0036 for the polycrystalline DPPH.[7] The static magnetic field was measured by proton resonance with an error of less than 0.3 Oe.

III. ANALYSIS OF DATA

A thorough knowledge of F-center characteristics is needed before any investigation of the Z_1 center can be begun. The Z_1-center optical absorption is never completely resolved from the F-center absorption; likewise the ESR data are found to be a mixture of F and Z_1 characteristics. Specimens of pure KCl were obtained from the Harshaw Chemical Company and the Isomet Corporation. Optical-absorption curves were taken at 300 and 77°K on samples colored either additively or by γ irradiation. The optical curves indicated that the base line of the F-center absorption was different from zero. The baseline shift corrections which were made were a long extrapolation of the K band and a gentle upward slope of the absorption from 2000 to 400 mμ. The corrected F-band absorption curve could be fit by a Gaussian curve within experimental error for the large central portion of interest. The product of the maximum absorption and band width is nearly the same at 300 and 77°K.

The F-band ESR was found in the limit of vanishing microwave magnetic-field strength. The large central portion fitted a derivative Gaussian curve with a peak-to-peak width of 49.3 Oe and a g value of 1.995, in agreement with the work of Holton and Blum.[8] The microwave fields were kept small to avoid saturation effects.

The combined F and Z_1 optical bands were observed near 300 and 77°K. With the assumption of a Gaussian shape for the Z_1 as well as the F band, the optical absorption is fitted by

$$\alpha_T=\alpha_{0F}\exp[-4(\ln 2)((h\nu-h\nu_{0F})/w_F)^2] +\alpha_{0Z_1}\exp[-4(\ln 2)((h\nu-h\nu_{0Z_1})/w_{Z_1})^2].$$

The ratio of the density of Z_1 centers to F centers is then calculated by applying Smakula's equation[9] to each of the absorption bands with an oscillator strength of 0.81 for the F band[10,11] and 0.84 for the Z_1 band.[12] At room temperature the Z_1 band parameters of Camagni and Chiarotti were used, but at liquid nitrogen temperature it was necessary to determine these parameters. A small F-center absorption was subtracted successively until a best fit to a Gaussian curve remained; by this method the peak position and half-amplitude width of the Z_1 band at liquid-nitrogen temperature were found to be

$$h\nu_{0Z_1}=2.068\pm0.005 \text{ eV } (599 \text{ m}\mu),$$
$$w_{Z_1}=0.290\pm0.005 \text{ eV}.$$

The Z_1 to F-center density ratio calculated from the low-temperature results was 4% higher than that calculated from room temperature data.

When Z_1 and F centers are both present in the sample, the room temperature ESR absorption is similar to that of the F center alone. The location of the inflection point in the derivative of absorption appears to be unchanged, but the peak-to-peak width is somewhat greater (Table I). Because it has not been possible to prepare samples containing Z_1 centers without a comparable number of F centers, it is necessary to determine the Z_1 center characteristics by an extrapolation procedure. The experimental value of g and the total peak-to-peak width W_T are chosen as the ordinates of different plots. In both cases the fraction of Z_1 centers is chosen as the abcissa. If mostly F and Z_1 centers are present, then the fraction of Z_1 centers is $F_{Z_1}=N_{Z_1}/(N_{Z_1}+N_F)$.

The plot of g versus F_{Z_1} can be extrapolated as a straight line with zero slope, to a value of 1.9952 ±0.0005 (Fig. 2). Thus, the Z_1 center has a g value which is the same as or only slightly different from that of the F center.

The apparent width of the combined ESR curve is *not* a linear function of the fraction of Z_1 centers present. This result is demonstrated by the calculation described below, which depends on the following assumptions: (1) F and Z_1 centers have ESR absorption curves which are essentially Gaussian. (2) The oscillator strength for the Zeeman transition in the ground state is the same for both centers since the g values are equal. (3) There is

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[6] C. Hutchinson, R. Pastor, and A. Kowolski, J. Chem. Phys. **20**, 534 (1952).

[7] A. Holden, C. Kittel, F. Merrit, and W. Yager, Phys. Rev. **77**, 147 (1950).

[8] W. Holton and H. Blum, Phys. Rev. **125**, 89 (1962).

[9] A. Smakula, Z. Physik **59**, 603 (1930).

[10] G. Kleinschrod, Ann. Physik **27**, 97 (1936).

[11] R. H. Silsbee, Phys. Rev. **103**, 1675 (1956).

[12] P. Camagni, G. Chiarotti, F. Fumi, and L. Giulotto, Phil. Mag. **45**, 228 (1954).

TABLE I. F and Z_1 ESR data for additively colored specimens.

Sample No.	Impurity	Optical bands present	F_{Z_1}	T (°K)	W_T (Oe)	g	$_{1/2}M_0^+(H>H_0)$ (Oe)	$_{1/2}M_0^-(H<H_0)$ (Oe)
1	$SrCl_2$	$F+Z_1$	0.48_5	300	53	1.9945	48.1	40.6
2	$SrCl_2$	$F+Z_1$	0.49_5	300	53.4	1.9947	42.6	40.2
3	$SrCl_2$	F	0	300	49.3	1.9944	41.7	41.0
		$F+Z_1$	0.55	300	54.0	1.9957	44.1	41.5
4	$SrCl_2$	F	0	300	49.1	1.9957	41.5	38.4
5	None	F	0	77	50.1	1.9955	38.7	33.3
		F	0	300	49.1	1.9955	37.2	38.8

no saturation of either resonance (or if there is, the saturation is the same for both, i.e., the relaxation times must be equal.) The consequence of the last two assumptions is to make the F and Z_1 center concentrations directly proportional to the areas under the corresponding ESR curves. A linear combination of absorption curves may then be taken when both F and Z_1 centers contribute to the ESR:

$$A_T=N_F\exp[-2((H-H_0)/W_F)^2]+N_{Z_1}\exp[-2((H-H_0)/W_{Z_1})^2].$$

The apparent peak-to-peak width W_T found by maximizing the derivative of this absorption curve is given by

$$W_T{}^2=\frac{\exp[-\frac{1}{2}(W_T/W_F)^2]+(W_F/W_{Z_1})^3(F_{Z_1}/(1-F_{Z_1}))\exp[-\frac{1}{2}(W_T/W_{Z_1})^2]}{\dfrac{1}{W_F{}^2}\exp\left[-\dfrac{1}{2}\left(\dfrac{W_T}{W_F}\right)^2\right]+\dfrac{1}{W_{Z_1}{}^2}\left(\dfrac{W_F}{W_{Z}\text{-}}\right)^3\dfrac{F_{Z_1}}{1-F_{Z_1}}\exp\left[-\dfrac{1}{2}\left(\dfrac{W_T}{W_{Z_1}}\right)^2\right]}.$$

Roots for this implicit equation were determined by iteration on an IBM-650 computer for a number of values of the parameters. Both a general analysis of the equation and the numerical results indicate that only one set of peaks occurs in the derivative as long as $W_{Z_1}/W_F\leq 3.146$. There are, however, two sets of extrapolation curves for finding W_{Z_1}, and coupled with this is a forbidden region in which no points are found. (See Fig. 3.) The equation of the envelope is

$$7.170[(W_T/W_F)^2-1](W_T/W_F)^3\times\exp[-\tfrac{1}{2}(W_T/W_F)^2]=F_{Z_1}/(1-F_{Z_1}).$$

By plotting the observed widths on the extrapolation curves of Fig. 3, it is determined that the derivative peak-to-peak width of the Z_1 center is 63±1 or 87±5 Oe. Since the slope of the line connecting the experimental points is not sufficiently accurate to decide which result should be chosen, the half-zero moment must also be considered. The half-zero moment is the area under one side of the normalized derivative ESR

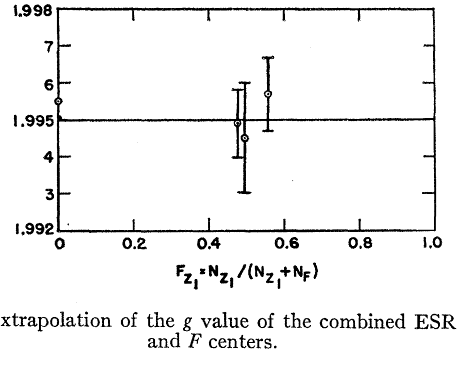
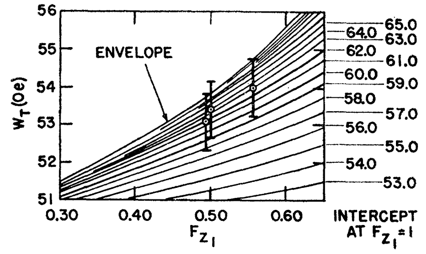
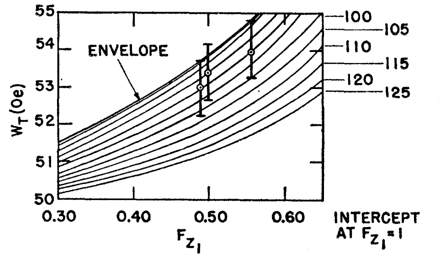


FIG. 2. Extrapolation of the g value of the combined ESR of Z_1 and F centers.



a. FIRST DEGENERACY



b. SECOND DEGENERACY

FIG. 3. Expanded combined ESR derivative width extrapolation curves for Z_1 and F centers.

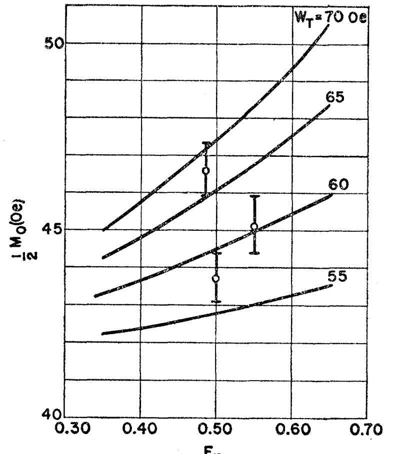


FIG. 4. Expanded ${}_{1/2}M_0$ extrapolation curves.

absorption.

$$ {}_{1/2}M_0^+ = \int_{H_0}^{\infty} \frac{\partial A}{\partial H} dH, \quad H_0 \leq H < +\infty , $$

$$ {}_{1/2}M_0^- = \int_{H_0}^{-\infty} \frac{\partial A}{\partial H} dH, \quad H_0 \geq H > -\infty . $$

A single derivative Gaussian has

$$ {}_{1/2}M_0^+ = {}_{1/2}M_0^- = {}_{1/2}M_0 = \tfrac{1}{2}e^{1/2}W , $$

but the situation is more complicated whenever two species of derivative absorptions are considered. When both contributions have the same g value, it is found that

$$ {}_{1/2}M_0 = (1+(W_F/W_{Z_1})(F_{Z_1}/1-F_{Z_1})) \Big/ \left\{ \frac{2W_T}{W_F^2} \exp\left[-\frac{1}{2}\left(\frac{W_T}{W_F}\right)^2\right] + \frac{2W_TW_F}{W_{Z_1}^3} \frac{F_{Z_1}}{1-F_{Z_1}} \exp\left[-\frac{1}{2}\left(\frac{W_T}{W_{Z_1}}\right)^2\right] \right\} . $$

The measured ${}_{1/2}M_0$ of the F center is slightly smaller than the value calculated from the width because a small, broad, spurious resonance on the low-field side tends to make the tail of this side smaller.

$$ |{}_{1/2}M_0|_{\text{calc}} - |{}_{1/2}M_0|_{\text{exp}} = 40.6 - 38.3 = 2.3 \text{ Oe}. $$

Hence, 2.3 Oe is taken as a correction to be added to the measured values of ${}_{1/2}M_0$ for the combined F and Z_1 center resonances. The corrected and averaged values of ${}_{1/2}M_0$ for the combined ESR are plotted in Fig. 4; the points fall in the region of curves determined by $W_{Z_1} = 62 \pm 3$ Oe. Thus, the lower value of the Z_1 center resonance width is to be selected.

A preliminary study of the magnetic resonance of the Z_2 center was also made in order to estimate the influence that a Z_2 admixture might have upon the combined F and Z_1 center ESR spectrum. The Z_2 optical band is observed to grow spontaneously at room temperature in the dark in a sample of KCl initially containing only F and Z_1 bands; a noticeable contribution to both the optical and ESR absorption is detectable after about 20 h. A KCl crystal with $SrCl_2$ impurity which had been used in the Z_1 center studies was selected, and the Z_2 band was developed by alternately bleaching at 500 mμ and heating to 75°C to destroy the Z_1 band. The relative optical-absorption amplitudes of the Z_2 and F band at liquid-nitrogen temperature were approximately equal. The derivative ESR absorption of the sample was determined at room temperature and had the parameters:

$$ g = 1.9962 \pm 0.0002, \quad {}_{1/2}M_0^- = 70 \text{ Oe}, \quad (H < H_0), $$
$$ W_T = 58 \pm 2 \text{ Oe}, \quad {}_{1/2}M_0^+ = 39 \text{ Oe}, \quad (H > H_0). $$

This particular spectrogram was determined twice; although both charts were noisy, the essential characteristics were the same.

IV. DISCUSSION OF RESULTS

The ESR parameters for the Z_1 centers found in this investigation are a peak-to-peak width of 63 ± 1 Oe and a g value of 1.9952 ± 0.0005. A Gaussian line shape is strongly inferred.

The ESR experiment with Z_1 centers has also been performed by Kawamura and Ishiwatari.[13] Their results for Z_1 centers using $SrCl_2$ in KCl are a half-amplitude width of 79 ± 8 Oe (corresponding to a peak-to-peak width of 67 ± 7 Oe for a derivative Gaussian curve) and a g value of 1.9991 ± 0.005. Possible explanations of these discrepancies are preferential saturation of the ESR absorptions or dark formation of Z_2 centers. Preferential saturation would not account for the g value discrepancy. Perhaps the Z_2 center formation would, for, as shown in Sec. III, the combined ESR of F and Z_2 centers is very asymetrical with the low-field side being emphasized. This would mean $g_{Z_2} > g_{Z_1}$. Furthermore, the $\{F,Z_2\}$ resonance is of about the same width as that found for the $\{F,Z_1\}$ resonance by Kawamura and Ishiwatari ($F_{Z_1} \approx 0.55$, $W_T = 57 \pm 3$ Oe peak-to-peak). These values plot in the forbidden region of the width extrapolation curves in Fig. 3. An awareness of the thermal equilibrium conditions for Z_2 centers is lacking in the literature of the 1956 to 1957 period.

The observed ESR parameters may be considered in terms of the current models. In a qualitative way, the fact that the F and Z_1 ESR results both give the same g value tends to favor Seitz's model of the Z_1 center, for the symmetry of this model is the same as for the F center. The less symmetrical model of Pick would be

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[13] H. Kawamura and K. Ishiwatari, J. Phys. Soc. Japan **13**, 547 (1958).

expected to give a larger amount of $\mathbf{L}\cdot\mathbf{S}$ interaction than the F center and, hence, a greater change in g value.

In the next section, an attempt is made to estimate the width of the ESR signal to be expected for the Z_1 center on the basis of Seitz's model. It will be seen that the calculations are not sufficiently well refined to allow a positive identification of this model with the Z_1 center. It is encouraging to see, however, that seemingly reasonable forms of the Z_1-center wave function are, indeed, consistent with the observed results.

V. ESTIMATE OF WIDTH OF Z_1 CENTER RESONANCE

The width of the ESR signal for all color centers is presumably caused by unresolved hyperfine interaction between the trapped electron and the neighboring nuclei. The primary contribution to the second moment of the ESR line comes from the isotropic or contact hyperfine interaction with the first- and second-nearest neighbors, and this is the only effect that is considered here. The energy for an electron spin transition, as obtained to first order from the usual spin Hamiltonian, is

$$\Delta E = g\beta H + \sum_k a_k m_k = \hbar\omega = g\beta H_0,$$

where m_k is the z component of the spin of nucleus k, ω is the frequency of the microwave spectrometer, and H_0 is the value of the magnetic field at the center of the ESR line. The hyperfine interaction constant a_k is given by

$$a_k = \frac{16\pi}{3}\beta\beta_N\frac{\mu_k}{I_k}A_k|\psi_E(\mathbf{r}_k)|^2,$$

where β and β_N are the Bohr and nuclear magnetons, μ_k and I_k are the magnetic moment and spin of nucleus k, and $\psi_E(\mathbf{r}_k)$ is the electron wave function at the location of nucleus k. A_k is an amplification factor that must be introduced because the envelope wave function $\psi_E(\mathbf{r}_k)$ is not orthogonal to the wave functions of the ion core electrons surrounding nucleus k[14]; this factor is discussed in more detail below. The second moment of the ESR line is obtained from the expression for ΔE.

$$M^{(2)} = \langle (H-H_0)^2\rangle_{\text{av}} = \frac{1}{(g\beta)^2}\sum_k a_k^2\frac{I_k(I_k+1)}{3}.$$

The square root of $M^{(2)}$ is equal to half the peak-to-peak width for the derivative of a Gaussian curve.

In order to evaluate the a_k and, hence, $M^{(2)}$ for the Z_1 center, it is necessary to determine not only the envelope wave function ψ_E but also the amplification factors A_k. Kawamura and Ishiwatari have calculated $A_{\text{K}}=470$ and $A_{\text{Cl}}=320$ by using cellular wave functions for KCl and orthogonalizing these to the ion core orbitals.[13] We have preferred to use the following procedure, which should allow a fairly reasonable comparison between the F and Z_1 resonances. Directly measured values of A_{K} and A_{Cl} obtained from ENDOR experiments on F centers in KCl by Holton and Blum[8] are used along with a calculated envelope wave function for the F center to evaluate A_{K} and A_{Cl}. Then the same values of A_{K} and A_{Cl} are used with a calculated envelope wave function for the Z_1 center to determine the a_k and, thence, $M^{(2)}$ for the Z_1 ESR absorption.

The procedure outlined above is based on the assumption that the value of A_k for a particular ion depends only on the wave functions of the ion core electrons surrounding nucleus k but not on the wave function of the trapped electron. This assumption can be approximately justified on both empirical and theoretical grounds. Experimental results of ENDOR measurements for F centers in a number of alkali halide crystals lead to values of A_k which are consistent for a given ion within 10 or 15%.[8] The theoretical expression for A_k is obtained by assuming that the envelope wave function varies slowly over the region occupied by each of the surrounding ions[15]; since the general shape of the F and Z_1 center wave functions must be rather similar, namely, a symmetric function concentrated within a few atomic spacings, this assumption should be nearly as valid for the Z_1 as for the F center. The expression for A_k also contains the overlap integrals between the trapped electron and the ion core wave functions explicitly in a normalization factor. The contributions from the surrounding ions should be comparable for F and Z_1 centers for the reason given above, but the central divalent ion in the Z_1 center will contribute an additional amount, which according to a very rough calculation is approximately 30% of the normalization factor. Hence, the values obtained for the A_k from F center measurements should be approximately valid for all ions surrounding the Z_1 center except for the central divalent ion. Since the nucleus of this ion does not contribute to the second moment of the Z_1 resonance, as discussed below, the procedure presented here should be appropriate within the indicated limits of approximation.

The calculation, then, involves making an estimate of envelope wave functions for the F and Z_1 centers, and to be consistent with the spirit of the calculation, which is basically a comparison procedure, the same general viewpoint and methods should be used for both centers. The simplest approach to calculating the envelope wave functions is to use a continuum model; in this case both the F and Z_1 centers are represented by a positive point charge embedded in a dielectric medium. The effective mass is taken equal to the free-electron mass for lack of more specific information, and the high-frequency dielectric constant, which is the part caused by electronic polarizability, is used throughout the calculations ($\epsilon=2.10$). In this approach, it is found that $A_{\text{K}}=860$

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

[15] B. S. Gourary and F. J. Adrian, Phys. Rev. **105**, 1180 (1957).

and $A_{\text{Cl}}=1400$, in fairly good agreement with Gourary and Adrian's calculated values of 640 and 1500,[14] but the predicted peak-to-peak width for the Z_1 ESR is 153 Oe, which is much too large. A brief inspection of the models reveals why this is so: The chlorine nuclei, with mean square magnetic moment $\langle\mu_{\text{Cl}}\rangle=0.790$ compared to $\langle\mu_{\text{K}}\rangle=0.382$, are nearest neighbors of the Z_1 center but only next nearest neighbors of the F center.

It is also clear by inspecting the models that the negatively charged electron will tend to stay away from the Cl^- ions near the Z_1 center and be attracted by the K^+ ions near the F center, thus reducing the discrepancy. In an attempt to incorporate some of these features of the atomic surroundings, the first stages in a perturbation calculation have been carried out. The potential is taken to be the electrostatic point ion potential modified by the high-frequency dielectric constant. For hydrogen-like wave functions, matrix elements have been evaluated explicitly up to and including the 6*s* wave function, but the continuum has not been included. Since there is only one bound *s* state for the square well potential (and only one bound *p* state at zero energy), an integration over the continuum has been carried out for this case with only one small approximation. The most suitable zero-order potential for the F center is a square well; with the unperturbed wave-function values of $A_{\text{K}}=355$ and $A_{\text{Cl}}=649$ are obtained. With a single positive charge as the zero order potential for the Z_1 center, the calculated width is found to be $W_{pp}=67$ Oe, but the apparent agreement with the experimental value must be somewhat fortuitous. With first-order corrections to the F center wave function, for instance, $W_{pp}=41$ Oe, with similar corrections for the Z_1 center $W_{pp}=30$ Oe, and with first-order corrections for both centers $W_{pp}=19$ Oe. Kawamura and Ishiwatari obtain $W_{pp}=37$ Oe,[13] but their value for A_{Cl} appears to be too small.

Another interesting aspect of the calculations is the possibility of a hyperfine interaction with the divalent ion at the heart of the Z_1 center. Most of the isotopes of Sr have zero nuclear spin and magnetic moment, but Sr^{87}, with a natural abundance of 7.02%, has $I=\frac{9}{2}$ and $\mu=-1.09\beta_N$. The value of the wave function at the nucleus may be estimated for this case by means of the Fermi-Segrè-Goudsmit expression[16,17]:

$$|\phi(0)|^2=\frac{1}{\pi a_0^3}\frac{Z_iZ_0^2}{n_e^3}\frac{1-(ds/dn)}{(1-\alpha^2Z_i^2)^2}.$$

Z_i is equal to the charge on the nucleus for a penetrating *s* electron, Z_0 is the outer charge seen by the electron when it is outside the ion, n_e is the effective quantum number in a Rydberg-Ritz expression for the energy $E_n=-RZ_0^2/n_e^2$, s is the quantum defect in $n_e=n-s$, a_0 is the radius of the first Bohr orbit, α is the fine structure constant, and R is the Rydberg energy. This expression is quite successful in predicting hyperfine structure for free atoms and ions,[18] and it may be used for the continuum model of the Z_1 center with the following modifications. The inner charge Z_i and the relativistic correction $(1-\alpha^2Z_i^2)^{-2}$ are unchanged, $Z_0=\epsilon^{-1}$ according to the continuum model, $n_e=1.03$ is obtained from the optical-transition energy of 2.11 eV by using the first two terms of a Rydberg-Ritz series and assuming s to be constant, and $1-(ds/dn)$ is accordingly set equal to 1 for lack of additional data.[19] The result gives $a_{\text{Sr}}=560$ mC $=200$ Oe. This value is sufficient to remove the resonance signal for Z_1 centers containing Sr^{87} from the central resonance line (half-width 32 Oe), and, therefore, this effect has not been included in evaluating the second moment for the Z_1 center resonance. No resolved hyperfine structure was observed in the present work because of the 140-fold reduction in intensity compared to the main ESR signal, but striking effects should appear in ENDOR measurements.

It is felt that the present approach gives a fairly reasonable picture for the F center, largely because the trapped electron spends most of its time in the vacancy where no other electrons are present. The Z_1 center calculations are much less reliable because of the presence of the divalent ion core in the central region and the rather diffuse negative ion cores as nearest neighbors. It is hoped that the Z_1 center calculations can be improved by developing a better method for describing the divalent ion, perhaps by means of an effective potential.

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

[17] S. Goudsmit, Phys. Rev. **43**, 636 (1933).

[18] The calculated value of the hyperfine splitting for the $5s\ ^2S_{1/2}$ state in Sr^+ is -0.175 cm^{-1}, and the observed value is -0.165 cm^{-1} {A. G. Zhiglinskii and G. G. Kund, Opt. i Spektroskopiya **7**, 490 (1959) [translation: Opt. Spectry. USSR **7**, 490 (1959)]}.

[19] For the free Sr^+ ion, this factor has a value 1.04 according to the energy levels given by C. E. Moore, Nat. Bur. Std. (U. S.) Circ. **467**, 191 (1952).