

ON THE THEORY OF THE ELECTRON SPIN RESONANCE OF F-CENTERS IN CRYSTALS WITH NaCl STRUCTURE

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Two models of the F center are used, the de Boer and the Hilsch-Pohl models. The wave function of the ground state is derived for both models, using the molecular orbital approximation. The hyperfine interaction of the F-center electron with the magnetic moments of the nuclei in the first and second coordination spheres is considered. The coupling constants in the corresponding spin Hamiltonian are calculated. The paramagnetic resonance absorption of radio-frequencies by F centers is examined. The shape and width of the absorption band are obtained. For the KCl crystal, comparison with the experimental data shows agreement of theory and experiment.

INTRODUCTION

THE paramagnetic absorption of radio frequencies by F centers was experimentally discovered by Hutchison.^{1,2} The results were interpreted theoretically by Kip et al.,³ using the de Boer model, according to which the F center is a negative ion vacancy at which an electron is located. The quantum-mechanical description of the F center in reference 3 was made on the basis of the molecular orbital approximation, developed in reference 4. Kip et al. did not take into account the overlap of the eigenfunctions of adjacent ions, as a consequence of which the variation of absorption frequency with crystal orientation relative to the external static magnetic field (the paramagnetic absorption anisotropy effect) is left out. The existence of such a variation was emphasized by Deĭgen and the author.^{5,6} The variation was experimentally discovered by Feher,⁷ and a detailed theoretical interpretation of the results was obtained by Deĭgen and Zevin.⁸

Kip et al.³ introduced into the coupling constant of the spin Hamiltonian a parameter that was determined by a comparison of the theoretical and experimental values of the absorption bandwidth. In references 5, 6, and 9 a method is proposed for calculating, in the macroscopic approximation¹⁰ for the F center, the coupling constants in the spin-Hamiltonian which describes the interaction of the F-center electron (de Boer model) with the magnetic moments of the nuclei in the first and second coordination spheres surrounding the halide vacancy. Glinchuk and Deĭgen¹¹

considered the F-center in the macroscopic approximation using the Hilsch-Pohl model, according to which the F center is a surplus metallic ion at which an electron is located.

The coupling constants in the spin-Hamiltonian are calculated for the F center below (Sec. 2), taking into account the overlapping of the adjacent ion eigenfunctions in the molecular orbital approximation. The theory is parameterless and permits a comparison of the calculated values with experiment.^{7,8} In Sec. 3 the theory of radio wave absorption by F centers is developed for the Hilsch-Pohl model (molecular orbital approximation). The character of the resonance spectrum is qualitatively different for the two models, a fact already remarked on by other authors.^{11,12} The possibility therefore exists of deciding from the absorption band shape on the model for F centers in crystals; this is of great importance for silver halides, for example.

1. GROUND STATE OF THE F CENTER

De Boer Model. The wave equation of an electron located at a halide vacancy can be written in the form

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + \sum_k V_k(\mathbf{r} - \mathbf{R}_k) + \sum_l V_l(\mathbf{r} - \mathbf{R}_l) - \frac{e^2}{r} \right] \Psi = E\Psi. \quad (1)$$

The adiabatic approximation has already been used in this. Equation (1) is the electronic part of the general Schrödinger equation. The nuclei surrounding the vacancy are assumed fixed. Here \mathbf{r} is the distance from electron to vacancy, \mathbf{R}_k is the dis-

tance from the vacancy to the k -th positive ion, R_l is the analogous distance for the l -th negative ion, $V_k(\mathbf{r} - \mathbf{R}_k)$ is the potential energy of interaction with the k -th positive ion, $V_l(\mathbf{r} - \mathbf{R}_l)$ is the potential energy of interaction with the l -th negative ion, and $-e^2/r$ is the potential energy of interaction with the positive vacancy. Polarization of the dielectric by the electron is not taken into account.

To find the approximate solution of Eq. (1) we use the variational method. We consider only the electron interaction with the six positive and twelve negative ions nearest to the vacancy.

The energy of the ground state of the system E is determined from the minimum of the function

$$\int \Psi^* \hat{H} \Psi d\tau, \quad \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + \sum_{k=1}^6 V_k + \sum_{l=1}^{12} V_l - \frac{e^2}{r},$$

and we use the approximation function customarily employed in the molecular-orbital method,

$$\Psi = N \left[\sum_{k=1}^6 \psi_k + \gamma \sum_{l=1}^{12} \psi_l \right], \quad (2)$$

$$\int |\Psi|^2 d\tau = 1 \quad (3)$$

where N is a normalizing factor, ψ_k are the normalized eigenfunctions of the isolated atoms in the first coordination sphere, ψ_l are the normalized eigenfunctions of the ions in the second coordination sphere, and γ is the approximation parameter.

We substitute (2) in the variational integral, determine N from (3) and find the parameter γ from the equation $\partial E / \partial \gamma = 0$. In calculating the coefficients entering into the latter equation, we neglect "three-center" integrals (for example, $\int \psi_k V_{k'} \psi_l d\tau$, $k \neq k'$) and also omit terms with $l \neq l'$ by virtue of the rapid fall-off of ψ_l . The calculations on the Hilsch-Pohl model are carried through in the same approximation. The evaluation of the variational integral is simplified if the functions ψ_k and ψ_l , and the potentials V_k and V_l are represented by sums of Gaussian exponentials.

$$\begin{aligned} \psi_k(\rho_k) &= \frac{1}{\sqrt{4\pi}} \sum_i b_i \exp\{-\beta_i \rho_k^2\}, \\ \psi_l(\rho_l) &= \sum_m b_m \exp\{-\beta_m \rho_l^2\}, \\ V_k(\rho_k) &= \sum_p C_p \exp\{-\delta_p \rho_k^2\}, \quad V_l(\rho_l) = \sum_q d_q \exp\{-\varepsilon_q \rho_l^2\}, \\ \rho_k &= \mathbf{r} - \mathbf{R}_k, \quad \rho_l = \mathbf{r} - \mathbf{R}_l. \end{aligned} \quad (4)$$

For numerical calculation we use V_k for the K^+ ion from reference 13, and V_l for the Cl^-

ion from reference 14; for ψ_k we use the Hartree function with exchange for the 4s electron in the K atom,¹⁵ and for ψ_l the function obtained in reference 14. The error involved in approximation (4) does not exceed 3 or 4% for ψ_k and V_k , and 5 or 6% for ψ_l and V_l . Calculations for the KCl crystal lead to the value of the coefficient $\gamma = -0.08932$, which corresponds to the lowest value of the energy.

Hilsch-Pohl Model. We write the wave function of the electron captured by the additional positive ion in the crystal in the form

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_0 + \sum_k V_k + \sum_l V_l \right] \Psi = E \Psi, \quad (5)$$

V_0 is the interaction potential energy of the electron with the additional positive ion; V_k and V_l have the same meanings as before. We neglect the displacement of the ions by the interstitial atom.

The energy of the ground state of the system E is determined by minimizing the variational integral.

$$\int \Psi^* \hat{H} \Psi d\tau, \quad \text{where } \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + \sum_{k=1}^4 V_k + \sum_{l=1}^4 V_l + V_0,$$

i.e., we consider only the interaction of the electron with the interstitial ion and with the four positive and four negative ions of the lattice nearest to it. As the approximate wave function we take the following:

$$\Psi = N \left[\psi_0 + \delta_1 \sum_{k=1}^4 \psi_k + \delta_2 \sum_{l=1}^4 \psi_l \right], \quad \int |\Psi|^2 d\tau = 1. \quad (6)$$

ψ_0 is the wave function of the interstitial atom; ψ_k and ψ_l have the same meaning as previously; δ_1 and δ_2 are the parameters of the approximation. Substituting (6) in the variational integral and determining N from the normalization conditions we find δ_1 and δ_2 from the equations $\partial E / \partial \delta_i = 0$ ($i = 1, 2$). The integrals were evaluated using the previous approximations (4). For the KCl crystal with interstitial K^+ ion we find $\delta_1 = -0.3048$ and $\delta_2 = -0.02639$. These parameters correspond to the lowest value of the energy.

2. ELECTRON SPIN RESONANCE OF THE F CENTER. DE BOER MODEL

Following references 5, 6, 8, and 16, the spin-Hamiltonian describing the interaction of the localized electron with the magnetic moments of the six nuclei of the first coordination sphere can lead to the form

$$\hat{H}_s' = \sum_{k=1}^6 [A_k (\mathbf{I}_k s) + B_k (\mathbf{I}_k \mathbf{R}_k) (s \mathbf{R}_k)], \quad (7)$$

where

$$A_k = a_k + A_{22k}, \quad B_k R_k^2 = A_{33k} - A_{22k},$$

$$a_k = 4\pi \frac{\mu_k}{sI_k} |\Psi(\rho_k = 0)|^2, \quad A_{ppk} = \frac{\mu_k}{sI_k} \int \frac{x_{pk}}{\rho_k^3} \frac{\partial}{\partial x_{pk}} |\Psi|^2 d\tau, \quad (8)$$

μ , μ_k , S , and I_k are the magnetic moments and spins of the electron and the k -th nucleus, respectively; $\rho_k = |\mathbf{r} - \mathbf{R}_k|$; the index $p = 1, 2, 3$ enumerates the axes of the Cartesian system of coordinates (the origin of coordinates is at the k -th site, and the x_{3k} axis is directed along \mathbf{R}_k); Ψ is the wave function of the electron.

Similarly, the spin-Hamiltonian describing the interaction of the localized electron with the magnetic moments of the twelve nuclei of the second coordination sphere can be written:^{8,9}

$$\hat{H}_s^{II} = \sum_{l=1}^{12} [A_l (\mathbf{I}_l S) + B_l (\mathbf{I}_l \mathbf{R}_l) (S \mathbf{R}_l) + C_l I_{lx_l} S x_l], \quad (9)$$

$$A_l = a_l + A_{22l}, \quad B_l R_l^2 = A_{33l} - A_{22l}, \quad C_l = A_{11l} - A_{22l},$$

$$a_l = 4\pi \frac{\mu_l}{sI_l} |\Psi(\rho_l = 0)|^2, \quad A_{ppl} = \frac{\mu_l}{sI_l} \int \frac{x_{pl}}{\rho_l^3} \frac{\partial}{\partial x_{pl}} |\Psi|^2 d\tau, \quad (10)$$

μ_l , I_l are the magnetic moment and spin of the l -th nucleus, and $\rho_l = |\mathbf{r} - \mathbf{R}_l|$. Here the Cartesian coordinate system is associated with the l -th site. We bear in mind the following relationships:⁸

$$2A_{22k} + A_{33k} = -a_k, \quad A_{11k} = A_{22k},$$

$$A_{11l} + A_{22l} + A_{33l} = -a_l. \quad (11)$$

For the wave function we will use (2) with the known parameter γ . We remark that, by ignoring the overlapping of the eigenfunctions of neighboring atoms, we arrive at the results of Kip et al.³ In fact, in this approximation:

$$A_{33k} = A_{22k}, \quad B_k R_k^2 = 0, \quad A_{22k} = -\frac{4\pi}{3} \frac{\mu_k}{sI_k} |\Psi(\rho_k = 0)|^2,$$

$$A_k = \frac{8\pi}{3} \frac{\mu_k}{sI_k} |\Psi(\rho_k = 0)|^2,$$

which agrees exactly with the result of reference 3. When the overlap of eigenfunctions is taken into account, the constants $B_k \neq 0$.

Substituting (2) in (8) and omitting small "three-center" integrals we obtain

$$A_{ppk} = \frac{\mu_k}{sI_k} N^2 \left[\sum_{n=1}^6 \int \frac{x_{pk}}{\rho_k^3} \frac{\partial}{\partial x_{pk}} \phi_n^2 d\tau + 2 \sum_{n \neq k} \int \frac{x_{pk}}{\rho_k^3} \frac{\partial}{\partial x_{pk}} (\phi_k \phi_n) d\tau \right.$$

$$\left. + 2\gamma \sum_{l=1}^{12} \int \frac{x_{pk}}{\rho_k^3} \frac{\partial}{\partial x_{pk}} (\phi_k \phi_l) d\tau + \gamma^2 \sum_{l=1}^{12} \int \frac{x_{pk}}{\rho_k^3} \frac{\partial}{\partial x_{pk}} \phi_l^2 d\tau \right]. \quad (12)$$

Similarly, substituting (2) in (10) and neglecting "three-center" integrals, we obtain

$$A_{ppl} = \frac{\mu_l}{sI_l} N^2 \left[\sum_{k=1}^6 \int \frac{x_{pl}}{\rho_l^3} \frac{\partial}{\partial x_{pl}} \phi_k^2 d\tau + 2\gamma \sum_{k=1}^6 \int \frac{x_{pl}}{\rho_l^3} \frac{\partial}{\partial x_{pl}} (\phi_k \phi_l) d\tau \right.$$

$$\left. + 2\gamma^2 \sum_{m \neq l} \int \frac{x_{pl}}{\rho_l^3} \frac{\partial}{\partial x_{pl}} (\phi_l \phi_m) d\tau \right.$$

$$\left. + \gamma^2 \sum_{m=1}^{12} \int \frac{x_{pl}}{\rho_l^3} \frac{\partial}{\partial x_{pl}} \phi_m^2 d\tau \right]. \quad (13)$$

To perform the integrations in (12) and (13), approximations (4) are convenient, as well as the approximations for $\psi_k^2(\rho_k)$ and $\psi_l^2(\rho_l)$ used previously,^{6,9} thus the coefficients in the spin Hamiltonian of the first and second coordination spheres can be calculated.

We take the external static field along the z axis; then, as in reference 5, we have for the eigenvalues

$$H_s = s_z \left[\sum_{k=1}^6 \Delta_k I_k + \sum_{l=1}^{12} \Delta_l I_l \right],$$

$$\Delta_k = [A_k^2 + B_k R_k^2 \rho_k^2 (2A_k + B_k R_k^2)]^{1/2},$$

$$\Delta_l = [A_l^2 + B_l R_l^2 m_l^2 (2A_l + B_l R_l^2) + C_l n_l^2 (2A_l + C_l)]^{1/2}. \quad (14)$$

Here \mathbf{H} is the magnitude of the static magnetic field; ρ_k , m_l , n_l are the cosines of the angles between \mathbf{H} and \mathbf{R}_k , \mathbf{R}_l , x_l , respectively. The positions of the individual lines in the absorption band are determined by the equation

$$\hbar\Omega = \sum_{k=1}^6 \Delta_k I_k + \sum_{l=1}^{12} \Delta_l I_l \quad (\Delta I_k = \Delta I_l = 0, \quad \Delta S_z = \pm 1). \quad (15)$$

From (14) and (15) we can see the dependence of absorption frequency on crystal orientation relative to the external magnetic field.

In crystals of MgO the interaction of the F-center electron with only one magnetic moment, Mg^{25} , has been observed;¹⁷ the other nuclear magnetic moments in the first coordination sphere were zero. In this case the angular dependence of the line position has the form

$$\hbar\Delta\Omega = [A_k^2 + B_k R_k^2 \rho_k^2 (2A_k + B_k R_k^2)]^{1/2}, \quad (16)$$

where $\Delta\Omega$ is the separation between two adjacent lines. In reference 17 an empirical dependence of this separation on angle is given:

$$\hbar\Delta\Omega = a + b(3\rho_k^2 - 1). \quad (17)$$

By comparing (16) and (17) from a and b we determine A_k and $B_k R_k^2$. From (16), using the values found for the coefficients A_k and $B_k R_k^2$, we are satisfied that within the limits of experimental error the empirical angular dependence agrees with our formula (16).

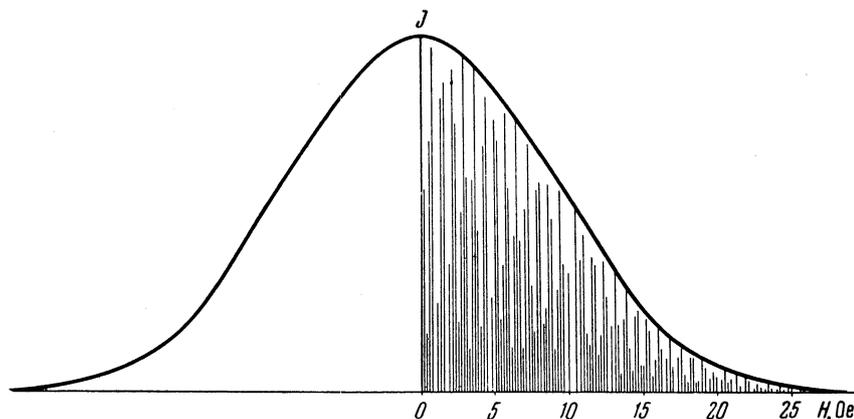


FIG. 1. Shape of the absorption band in KCl crystal (de Boer's model of the F center). The component lines are shown in only one half of the peak.

In references 5 and 6, it was emphasized that the absorption band shape differs somewhat from Gaussian, since I_k and I_l in (15) have different weighting factors. The calculations show that for the crystals considered, the constants $B_k R_k^2$, $B_l R_l^2$ and C_l are several times smaller than the corresponding A constants. Therefore, we can write approximately

$$\hbar\Omega = A_k \left[\sum_{j=1}^6 I_j + x \sum_{i=1}^{12} I_i \right], \quad x = A_l / A_k. \quad (18)$$

The intensities of the lines are proportional to the statistical weights of the energy states. We calculated the statistical weights using formula (18) for $I_j = I_i = 3/2$. For KCl the line shape calculated using (18) is shown in Fig. 1 (only the most intense lines, corresponding to the largest statistical weights, are shown in the given range of magnetic field). The envelope of these most intense lines is almost Gaussian. The half-width of the absorption band, as is known, is determined by the formula

$$\Delta h_{1/2} = 2 \sqrt{\frac{\ln 2}{\alpha} \frac{A_k}{\mu}} = 3.37 \frac{A_k}{\mu}, \quad (19)$$

where α is the parameter of the Gaussian approximation to the absorption band. The maximum width, taking into account the contribution of the second coordination sphere, in unit magnetic field is

$$\Delta h_m = (9A_k / \mu) [1 + 2x]. \quad (20)$$

Here the constants $B_k R_k^2$, $B_l R_l^2$, and C_l have been left out.

By way of example, the coefficients of the spin-Hamiltonian were calculated for the first and second coordination spheres for the KCl crystal. The half-width and maximum width of the absorption for this crystal were determined from (19) and (20) respectively. These values are given in the table, where the following notation is introduced:

$$\delta = \frac{A_{11k}}{a_k} = -\frac{1+x}{3+x}, \quad \gamma_1 = \frac{A_{11l}}{a_l} = \frac{z-y-1}{z+y+3},$$

$$\gamma_2 = \frac{A_{22l}}{a_l} = -\frac{y+z+1}{y+z+3},$$

$$x = B_k R_k^2 / A_k, \quad y = B_l R_l^2 / A_l, \quad z = C_l / A_l.$$

It appears from the table that agreement with experiment is better for the molecular-orbital approximation than for the macroscopic approximation (see references 6, 8, and 9). Somewhat poorer agreement with experiment exists for the constants of the second coordination sphere than for the first, which can be explained by the too rapid decrease of the Ψ -function for Cl^{--} used by us.¹⁴ There is satisfactory agreement with experimental data for the ratio of the constants. If we take for $\psi_k^2(0)$, instead of the low Hartree value, the value obtained from radio-spectroscopic data, then $\Delta h_{1/2} = 33$ oersteds, which is already significantly closer to the experimental value.

3. ELECTRON SPIN RESONANCE OF THE F CENTER. HILSCH-POHL MODEL

The spin Hamiltonian describing the interaction of the electron located at the additional positive ion with the ions closest to it has the form

	Theory	Experiment*		Theory	Experiment*
A_k/h Mcs	8.134	20.65	Δh_m , Oe	80.30	218.4
A_l/h Mcs	2.176	6.66	δ	-0.3344	-0.363
x	0.2675	0.323	γ_1	-0.3433	-0.387
$\Delta h_{1/2}$, Oe	19.60	54	γ_2	-0.3110	-0.377

* $\Delta h_{1/2}$ from reference 3, all other data from references 7 and 8.

$$\begin{aligned} \hat{H}_s &= \sum_{k=1}^4 A_k (\mathbf{I}_k \mathbf{s}) + \sum_{l=1}^4 A_l (\mathbf{I}_l \mathbf{s}) + A_0 (\mathbf{I}_0 \mathbf{s}) + \sum_{k=1}^4 \sum_{pq} A_{pqk} I_{pk} S_q \\ &+ \sum_{l=1}^4 \sum_{pq} A_{pql} I_{pl} S_q + \sum_{pq} A_{pq0} I_{p0} S_q, \\ A_{pqj} &= \frac{\mu_j \mu_l}{s I_j} \int \frac{x_{pj}}{e^3} \frac{\partial |\Psi|^2}{\partial x_{ql}} d\tau, \\ A_j &= 4\pi \frac{\mu_j \mu_l}{s I_j} |\Psi(\rho_j = 0)|^2, \quad j = 0, k, l; \end{aligned} \quad (21)$$

μ_0 and I_0 are the magnetic moment and spin of the interstitial atom.

We use (6) as the wave function. From considerations of symmetry $A_{pqj} = 0$ for $p \neq q$. We take the x_{30} axis along a crystallographic axis, x_{20} along a [110] direction and x_{10} along another similar direction; then $A_{pq0} = 0$ ($p \neq q$) by virtue of the fact that $|\Psi|^2$ and ρ_0 are even with respect to x_{10} and x_{20} . Directing x_{3k} to the interstitial ion, x_{1k} along the [110] direction, and x_{2k} perpendicular to both these axes, it is easy to show that $A_{pqk} = 0$ ($p \neq q$), $A_{12k} = A_{21k} = A_{31k} = A_{13k} = 0$ by virtue of the fact that $|\Psi|^2$ and ρ_k are even with respect to x_{1k} . $A_{23k} = A_{32k} = 0$, which is easily shown by rotating the coordinate system about the x_{3k} axis by an angle of 120° . In the same way it can be shown also that $A_{pqj} = 0$ ($p \neq q$).

We proceed with our consideration, ignoring the overlap of the eigenfunctions of neighboring ions. Then (21) takes the form

$$\hat{H}_s = A_0 (\mathbf{I}_0 \mathbf{s}) + A_1 \sum_{k=1}^4 (\mathbf{I}_k \mathbf{s}) + A_2 \sum_{l=1}^4 (\mathbf{I}_l \mathbf{s}), \quad (22)$$

where

$$A_0 = \frac{2\mu_0 \mu_l}{3s I_0} N^2 \phi_0^2(0), \quad A_1 = \frac{2\mu_1 \mu_l}{3s I_1} N^2 \delta_1^2 \phi_k^2(0),$$

$$A_2 = \frac{8\pi}{3} \frac{\mu_1 \mu_2}{s I_2} N^2 \delta_2^2 \phi_l^2(0).$$

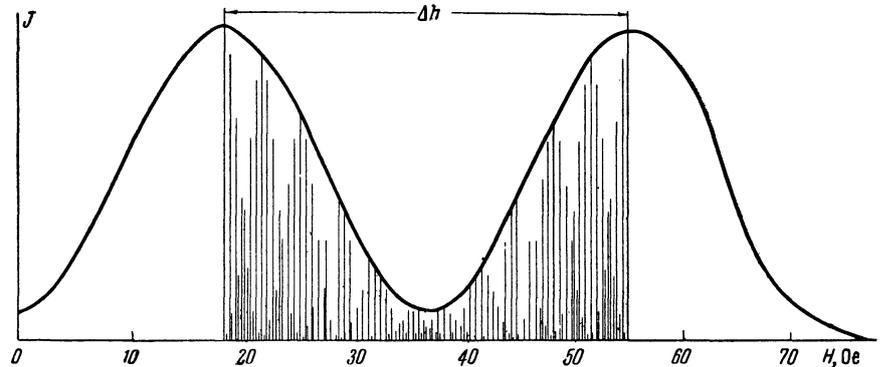
In the approximation considered $N = (1 + 4\delta_1^2 + 4\delta_2^2)^{-1}$.

Aligning the z axis with the direction of the static magnetic field and taking into account the selection rules ($\Delta I_{kz} = \Delta I_{lz} = \Delta I_{0z} = 0$, $\Delta S_z = \pm 1$) in complete analogy with (14) and (15), we obtain the position of the individual lines in the absorption band:

$$\begin{aligned} \hbar\Omega &= A_0 \left[I_{0z} + \alpha_1 \sum_{k=1}^4 I_{kz} + \alpha_2 \sum_{l=1}^4 I_{lz} \right], \\ \alpha_1 &= A_1 / A_0, \quad \alpha_2 = A_2 / A_0. \end{aligned} \quad (23)$$

The intensities of the lines are proportional to the statistical weights of the corresponding states calculated in reference 11. The shape of the band is shown in Fig. 2. In the band there are four max-

FIG. 2. Shape of the absorption band in KCl crystal (Hilsch-Pohl model of the F center). Only two maxima are shown, in each of which only the lines in one half are indicated. Two maxima omitted are disposed symmetrically relative to the origin of coordinates.



ima, corresponding to the interaction of the electron with the nuclear magnetic moment of the interstitial atom. Within the limits of each maximum the shape is close to Gaussian. The effective magnetic field, corresponding to the distance between two adjacent maxima, $\Delta h = A_0 / 2\mu$. The maximum width of the band (distance between the extreme lines in the spectrum) is

$$\Delta h_m = \frac{3}{2\mu} A_0 [1 + 4(\alpha_1 + \alpha_2)], \text{ oe.}$$

By way of example we calculated that for KCl with an additional K^+ ion, $\Delta h_m = 156$ oersteds,

$\Delta h = 36.4$ oersteds, $\kappa_1 = 0.09290$, and $\kappa_2 = 0.01461$. Since the distance between maxima is large and their overlap small, these four bands should be resolved experimentally. By the shape of the absorption band it should be possible to distinguish de Boer F centers from Hilsch-Pohl F centers.

In conclusion I express my sincere gratitude to M. F. Deigen for the suggestion of and constant interest in the work.

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