MAGNETIC RESONANCE STUDIES OF VACANCY CENTERS IN IONIC CRYSTALS

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1. INTRODUCTION

The application of magnetic resonance techniques to the study of paramagnetic centres has greatly improved our understanding of point defects. In fact ESR (Electron Spin Resonance) and especially ENDOR (Electron Nuclear Double Resonance) come close to what one may call an atomic scale microscopy of paramagnetic centres. In favourable cases one obtains a very detailed picture of the atomic structure of a defect (lattice site, neighbours, symmetry) including information about lattice distortions around the vacancy or the paramagnetic impurity, as well as detailed information about the electronic structure of the centre. This very precise picture of the paramagnetic defect is mainly the result of a careful determination of the strong hyperfine interaction (hf) between the unpaired centre electron and the centre nuclei as well as the weaker hf interaction with the nuclei of the surrounding lattice ions, (sometimes called "superhyperfine interaction", shf). In order to determine the latter, ENDOR measurements usually have to be performed, since they allow a much higher resolution of hf interactions compared to ESR measurements. Vacancy centres mostly contain no centre nuclei so that the shf interactions must be determined.

As early as 1949 ESR (1) and in 1961 ENDOR (2,3) measurements made decisive contributions to the determination of the structure of the F-centre in alkali halides, which consists of a single anion with one trapped electron, and finally confirmed the model originally proposed by De Boer (4). In the other ionic crystals like the alkaline earth oxides the identification of F type centres occurred first through ESR and ENDOR measurements, whereas their optical transitions were identified later.

It will be the purpose of the two lectures to discuss some results of ESR and ENDOR studies of a few vacancy centres with trapped electrons (sometimes also called electron excess centres or F-type centres) in some ionic crystals. It will not be possible within this limited scope to go into great detail and depth, nor will it be possible to present examples in all the ionic crystals where F-type centres have been studied. Somewhat arbitrarily most of the examples chosen are vacancy centres in the alkali halides. The discussion will be mainly concerned with the determination of the atomic structure of the vacancy centres. The question of the electronic structure can only be briefly touched. Relaxation phenomena and excited states will not be discussed.

For further information on the subject the reader is referred to review articles dealing with magnetic resonance of vacancy centres in the alkali halides (5), alkaline earth oxides (6,7) and alkaline earth fluorides (8).

2. ANALYSIS OF ESR AND ENDOR SPECTRA OF F-CENTRES

2.1. Spin Hamiltonian

F-like centres containing a simple electron in a vacancy have an orbitally nondegenerate ground state of mainly s-character with spin quantum number $s = \frac{1}{2}$. The electronic wave function is moderately delocalised and overlaps appreciably onto neighbouring ions. Since the electronic wave function is strongly exposed to the crystal field and no excited states are very close to the ground state, spin orbit effects are usually very small. Only through admixtures of neighbour ion orbitals because of the overlap of the F centre wave functions, does spin orbit coupling onto the neighbours show up in a small shift of the g-value relative to the free electron (5). This allows the use of a much simplified general spin Hamiltonian for the interpretation of the ESR and ENDOR spectra:

$$H = \underbrace{g\beta\vec{B}_o\vec{S}}_{H_{EZ}} + \underbrace{\sum_l \bigl(a_l\vec{S}\vec{I}_l + \vec{S}\tilde{B}_l\vec{I}_l}_{H_{SHF}} \underbrace{- g_{I,l}\beta_n\vec{B}_o\vec{I}_l}_{H_{NZ}} + \underbrace{\vec{I}_l\tilde{Q}_l\vec{I}_l\bigr)}_{H_Q} \quad (1)$$

H_{EZ} describes the electron-Zeeman-interaction (β is the Bohr magneton, $\vec{B}_o$ the applied magnetic field). H_{SHF} is the superhyperfine (shf) interaction between the F electron and the neighbouring lattice nuclei, H_{NZ} is the nuclear Zeeman interaction (β_n is the nuclear magneton, g_I the nuclear g-factor), and H_Q is the quadrupole interaction. The sum runs over all nuclei l of the lattice surroundings experiencing an interaction with the F-electron (in the alkali halides up to the 9th shell (9)) $\vec{S}$ and $\vec{I}$ represent the electron and nuclear spin operators. The hyperfine "contact" term a, or "isotropic shf constant" is proportional to the unpaired spin density at the nucleus of concern (index l omitted) (10):

$$a = \frac{2\mu_o}{3} g\beta g_I \beta_n |\psi(o)|^2 \qquad (2)$$

$\psi(r)$ is the wave function of the F electron, $\psi(o)$ its value at a particular nucleus of the lattice surrounding. The anisotropic shf interactions can be visualised as the classical dipole-dipole interactions of electron and nuclear moments averaged over the density distribution $|\psi|^2$ of the unpaired electron. $\tilde{B}_l$ is a traceless tensor with the elements

$$B_{ik} = \frac{\mu_o}{4\pi} g\beta g_I \beta_n \int_V \left(\frac{3}{r^5} x_i x_k - \frac{1}{r^3}\delta_{ik}\right) |\psi(\vec{r})|^2 dV \qquad (3)$$

$\vec{r}$ means the radius vector from the nuclear site of concern (origin) where the origin is spared in the integral Equ.3.

$\tilde{Q}$ is the traceless quadrupole interaction tensor with the elements

$$Q_{ik} = \frac{e\,Q}{2I(2I-1)} \left.\frac{\partial^2 V}{\partial x_i \partial x_k}\right|_{r = o} \qquad (4)$$

$\tilde{Q}$ contains the electrical field gradient at the nuclear site due to the total charge distribution in its neighbourhood.

For the analysis of spectra it is important to note that each neighbour nucleus has its own principal axes for the tensors of the shf (x', y', z') and quadrupole interaction (x", y", z"). The point symmetry of the nucleus may determine some or all of the principle axes (2). The nearest neighbours of the F-centre in alkali halides, for example, have their connection line to the

F centre as one principle axis, whereas the other two are equivalent (axial symmetry) and can be chosen in any direction perpendicular to it. Instead of the principle values of the tensors B and Q, the following quantities are often used:

$$b = \frac{1}{2} B_{z'z'} \qquad b' = \frac{1}{2} (B_{x'x'} - B_{y'y'}) \qquad (5)$$

$$q = \frac{1}{2} Q_{z''z''} \qquad q' = \frac{1}{2} (Q_{x''x''} - Q_{y''y''}) \qquad (6)$$

b and q respresent the axially symmetric part of the shf and quadrupole-tensors respectively, z' and z" are taken as the principle axes with the largest interaction. b' and q' describe the deviations from axial symmetry.

2.2. ESR Transitions

Using first order perturbation theory with the assumptions of high field ($g\ \beta\ B_o \gg a$) and small anisotropic interaction ($B_{ik} \ll a \pm g_I\ \beta_n B_o$) the eigenvalues of Equ. (1) are given by

$$\begin{aligned} E = {} & g\beta B_o m_s - g_I \beta_n B_o m_I + m_s m_I \left(a + b(3\cos^2\gamma - 1)\right) \\ & + \frac{1}{2} q (3\cos^2\gamma' - 1)\left(3m_I^2 - I(I+1)\right) \end{aligned} \qquad (7)$$

γ and γ', respectively, are the angles between the principal axes (z') and (z") and the magnetic field B_o (z). For simplicity only the shf interaction with one neighbour nucleus is considered in Equ.7. ESR transitions occur at magnetic field values B_{res} because of the selection rules $\Delta m_s = \pm 1$, $\Delta m_I = 0$ according to the following equation:

$$h\nu_{ESR} = g\beta B_{res} + m_I \left(a + b\ (3\cos^2\gamma - 1)\right) \qquad (8)$$

Since m_I has 2I + 1 values, one obtains a shf splitting of the ESR spectrum. The lines are equally spaced with a field separation of $(g\beta)^{-1}\left(a + b(3\cos^2\gamma - 1)\right)$. In the case of F centres the electron interacts with many nuclei, e.g. 6 nearest neighbour cations and 12 nearest neighbour anions in the alkali halides. For certain field directions or negligible anisotropic interactions the nuclei of one neighbour shell may be equivalent. Then Equ.8 becomes

$$h\nu_{ESR} = g\beta B_{res} + \sum_l M_I(l)\left(a(l) + b(l)(3\cos^2\gamma - 1)\right) \qquad (9)$$

where the total spin quantum number $M_I(1)$ of the 1 th shell of equivalent nuclei is given by

$$M_I(1) = \sum_{\beta=1}^{N} m_{I,\beta} = NI,\ NI - 1,\ \dots\ ,\ - NI \qquad (10)$$

N is the number of equivalent nuclei in the 1 th shell. The intensity of the M_I - shf - line depends, however, on the different statistical weights, corresponding to the number of possible combinations of the m_I to form M_I (5).

2.3. ENDOR - Transitions

In the ENDOR experiment one measures the nuclear spin resonance of the lattice nuclei which are coupled to the unpaired electron. The nuclear resonance is detected through the desaturation of the partially saturated ESR transition (2,11). ENDOR transitions usually occur in the range between 0,5 - 100 MHz in vacancy centre problems. The selection rule for ENDOR transitions is: $\Delta m_s = 0$, $\Delta m_I = \pm 1$.

In the first order perturbation theory, that is with the conditions

$$|B_{ik}|,\ |Q_{ik}| \ll |a \pm \frac{1}{m_s} g_I \beta_n B_o|$$

the ENDOR frequencies obtained from Equ.(1) for $S = \frac{1}{2}$ (as in F centres) are:

$$\nu^{\pm}_{ENDOR} = \left|\frac{1}{2h} W_{shf} \mp \nu_h \pm \frac{1}{h} m_q W_Q\right| \qquad (11)$$

with the following abbreviations:

$$W_{shf} = a + b\ (3\cos^2\gamma - 1) + b'\sin^2\gamma\cos 2\delta \qquad (12)$$

$$W_Q = 3\left(q(3\cos^2\gamma' - 1) + q'\sin^2\gamma'\cos 2\delta'\right) \qquad (13)$$

γ,δ and γ',δ' are the polar angles of B_o in the shf and quadrupole principal axis, respectively.

$$\nu_n = \frac{1}{h} g_I \beta_n B_o \qquad (14)$$

ν_n is the Larmor frequency of a free nucleus in the magnetic field $\vec{B}_o$

$$m_q = \frac{m_I + m'_I}{2} \qquad (15)$$

m_q is the average between the two nuclear spin quantum numbers which are connected by the transition. If no quadrupole interaction is present each interacting neighbour nucleus of the F centre gives according to Equ. (11) a pair of ENDOR lines. The two lines are separated by $2\nu_n$ if $\frac{1}{2h} W_{shf} > \nu_n$ and by $\frac{1}{h} W_{shf}$ if $\nu_n > \frac{1}{2h} W_{shf}$.

In case of non-vanishing quadrupole interactions each of the lines is split into quadrupole multiplets. Very often nuclei have nuclear spin $I = 3/2$, so that a symmetrical quadrupole triplet is observed. The "quadrupole lines" have a frequency separation of $\frac{1}{h} W_Q$ from the "shf-line". The simple first order solutions are very often not adequate to explain the details of the ENDOR spectra. Especially for larger anisotropic shf interactions and quadrupole interactions of the same order as shf interactions as well as stronger deviations from axial symmetry of the tensors, higher order perturbation theory or even a full diagonalisation of the Spin Hamiltonian Equ.(1) must be taken into account. For the F-centres in alkali halides second order perturbation theory is sufficient (9). One of the clearly visible effects of higher order corrections is e.g. that quadrupole triplets are no longer symmetric and the "shf-lines" are shifted by the quadrupole interactions. For further details of the analysis of ENDOR spectra the reader is referred to the literature (2, 12, 13, 14, 15, 16).

Basis for the assignment of ENDOR lines to certain neighbour nuclei is the careful analysis of the dependence of the ENDOR spectrum on the orientation of the magnetic field. An ENDOR spectrum is understood if the orientation of the principal axes and the interaction constants determined from some ENDOR lines describe fully the measured angular dependence. For the identification of a particular sort of neighbour nuclei the following criteria can also be used:

(i) the pairwise appearance of "shf" ENDOR lines according to Equ. (11) with separation $2\nu_n$ or $\frac{1}{h} W_{shf}$

(ii) repeated appearance of the ENDOR lines in the presence of several isotopes with a frequency ratio equal to the ratio of nuclear g-factors

(iii) further splittings because of quadrupole interactions.

The analysis of an ENDOR spectrum is usually an iterative process. The ENDOR method has certainly become a very powerful tool in determining the atomic structure of a point defect such as a vacancy centre. In practice, however, one first assumes a model for the defect and then tries to explain the ENDOR spectra on the basis of that model.

3. F CENTRES

3.1. ESR Spectra

Fig. 1 shows the ESR spectrum for F centres in CaF_2 for $B_0 || (110)$. The 7 equidistant shf lines with a field separation of 61 Gauss have within 5% an intensity ratio of 1:6:15:20:15:6:1. Such a shf structure is explained by 6 equivalent nuclei of $I = \frac{1}{2}$. With this spectrum a model for the F centre is consistent, where the unpaired electron occupies an F^-vacancy and the observed shf structure is due to 6 second nearest F neighbours at the corners of a regular octahedron, provided the anisotropic shf interaction is small compared to the isotropic interaction. The latter is noted in only a small angular dependence of the shf splitting. The nearest 4 Ca^{++} cations are not seen, since the concentration of Ca^{++} ions with nuclear moments (^{43}Ca) is too small.

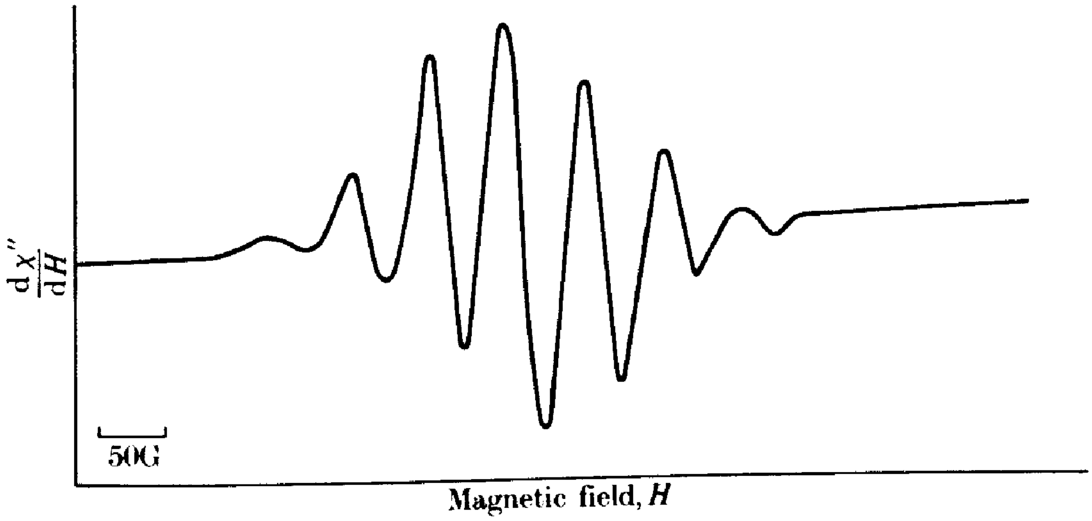

Fig. 1. ESR spectrum of F centres in CaF_2 at 300 K. $B_0 || (110)$. (after Arends (17)).

The ESR spectra of F centres in most alkali halides consist only of a single, broad line of Gaussian shape without further structure. The half width of the ESR line varies between about 50 to 750 G. In some cases (LiF, NaF, RbCl,CsCl) the line shows some shf structure, the analysis of which is not straightforward, however, so that from the ESR spectrum alone no safe conclusion on the centre model can be drawn. (5). The broad line arises because of "inhomogeneous broadening". The F electron interacts with so many neighbour nuclei that the shf structure is not resolved any more (5). The g factors are in all cases slightly smaller than the g-value of the free electron. The g-shift varies from 1 to about 500 x 10^{-4}, the shift increasingon going to crystals with heavier ions (19).

Analogous vancancy centres in the alkaline earth oxides show a nicely resolved shf structure. In these materials vacancy centres with one trapped electron are called F^+ centres. Fig.2 shows the ESR-spectrum in SrO for $B_o || (111)$. The alkaline earth oxides (except BeO) have the face centred cubic rocksalt structure and dominant ionic binding. The unpaired electron occupies an oxygen vacancy. In SrO it has 6 Sr^{++} ions as nearest neighbours. Only the ^{87}Sr has a magnetic moment and $I = \frac{9}{2}$. The strong line at $g_o = 1.9845$ is due to these 65% F^+ centres with only nonmagnetic ^{86}Sr and ^{88}Sr neighbours. For $B_o || (111)$ all nearest Sr nuclei are equivalent (there is only an isotropic shf interaction, since $\cos\gamma = \frac{1}{\sqrt{3}}$ in Equ. 8). If one Sr neighbour is ^{87}Sr, one expects 10 equidistant shf lines due to I = 9/2 which are observed, (line separation about 15 Gauss). About 5% of the centres will have two equivalent ^{87}Sr neighbours, which leads to 19 shf lines with the same splitting and a certain intensity ratio which can be clearly seen in the outer region of the spectrum. Between the lines just described further strong lines appear which were identified as forbidden transitions ($\Delta m_s = \pm 1$ and $\Delta m_I = \pm 1$) due to strong quadrupole interactions (7,20). The many details of the shf structure of the ESR spectrum allow a rather safe conclusion on the centre model and rather precise determination of the shf and quadrupole interactions.

3.2 ENDOR Spectra

Results of ENDOR investigations will briefly be discussed for F centres in alkali halides. Fig.3 shows the model of the F centre, which, of course, is the result of such an investigation, and Fig.4 shows the complete ENDOR spectrum of F centres in KBr for $B_o || (100)$: (2).

In the spectrum the shf and quadrupole interactions with 8 shells of neighbour nuclei are resolved in the frequency range between 0,5 and 30 MHz. All lines can be unambiguously assigned to nuclei

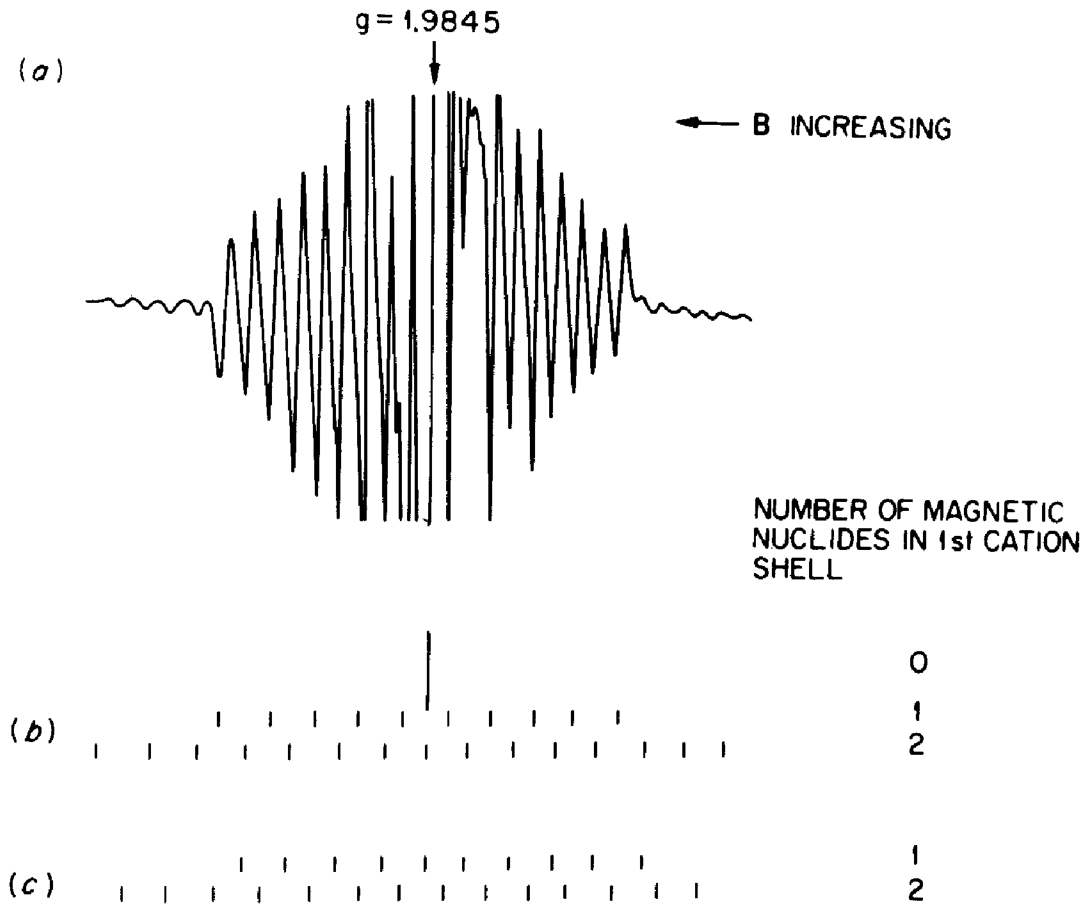

Fig. 2. a) ESR spectrum of F^+ centres in SrO for $B_o || (111)$
b) reconstruction of spectrum with 0,1 and 2 ^{87}Sr neighbours
c) forbidden transitions due to strong quadrupole interaction. The separation between vertical lines in b) and c) is about 15 G (after Culvahouse et al. (20)).

in the 8 shells. Following the principles briefly outlined in chapter 2 the spectrum can be analysed very precisely. The angular dependence of the first shell K neighbours is particularly simple and shown schematically in Fig. 5.

The angular dependence of ENDOR lines of higher shell nuclei is far more complicated. For a precise and unambiguous analysis of the spectra the magnetic field must be rotated in several planes. Fig.6 shows as an example the angular dependence of the ν^-_{ENDOR} lines (i.e. for $m_s = -\frac{1}{2}$) of shells V, VI, VIII and IX a (nuclei 003) in KCl (9). The solid curves are calculated using

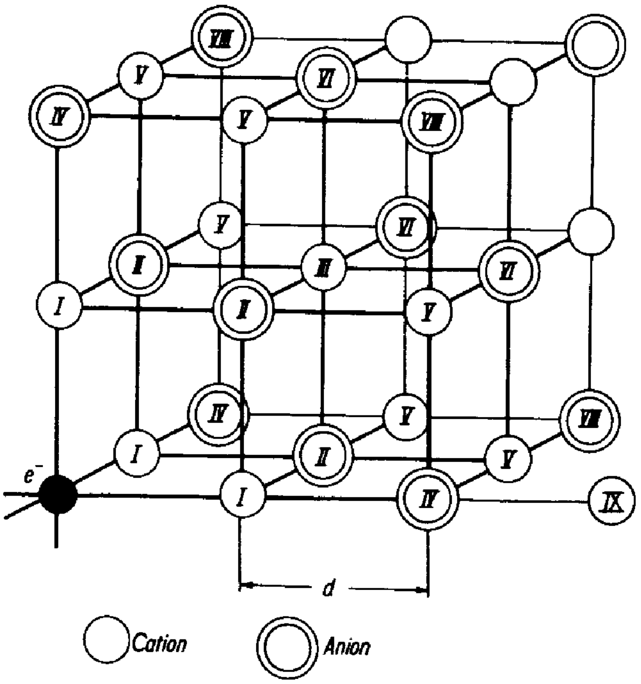

Fig. 3 Environment of the F centre with shells I - IX.

second order perturbation theory with the best set of interaction constants.

The results of the ENDOR analysis do not only confirm beyond any doubt the model of the F centre in the alkali halides as an electron trapped in an anion vacancy, but also yield very detailed information on the electronic structure by means of the shf and quadrupole interaction constants. Table 1 reproduces the results for F centres in KBr (2). Noteworthy is the high precision with which the interaction constants can be determined.

The quantitative results show that in the lower shells the shf interaction is predominantly isotropic. On going from shell I to about shell V there is a sharp drop in the shf interaction by about two orders of magnitude which tends to become more constant towards the higher shells (2,9). The interaction tensors have only very small deviations from axial symmetry where on pure symmetry arguments the axial symmetry is not required (shells II,V,VI,VII). Very detailed ENDOR investigations were also made on F centres in the alkaline earth fluorides (8) and on F^+ centres in the alkaline earth oxides (7).

Table 1 : shf interaction constants of the F centre in KBr in MHz (T = 90°K) (after Seidel(2)).

Shell	nucleus	a/h	b/h	3q/h
I	^{39}K	18.33	0.77	0.20
II	^{81}Br	42.85	2.73$^+$	0.23
III	^{35}Cl	0.274	0.022	
IV	^{81}Br	5.70	0.410	0.105
V	^{39}K	0.16	0.02	
VI	^{81}Br	0.838	0.082$^+$	
VIII	^{81}Br	0.583	0.068	

+ There is a small deviation from axial symmetry.

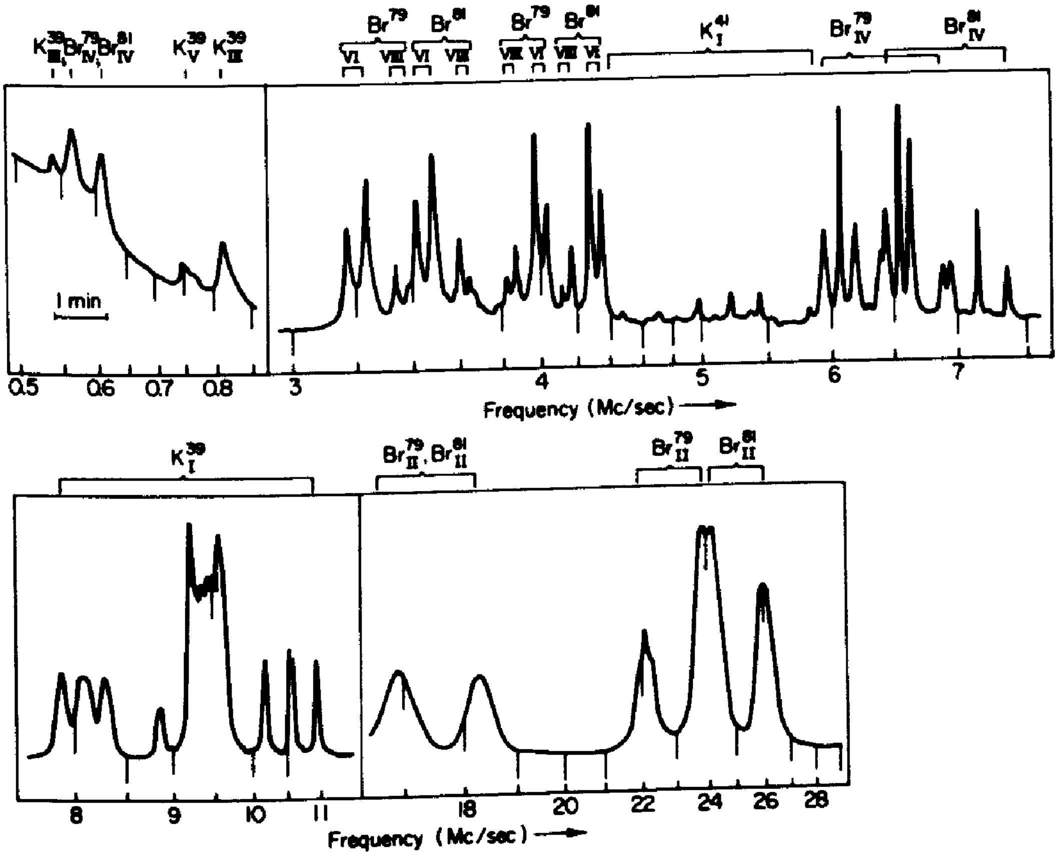

Fig. 4 ENDOR spectrum of F centres in KBr for $B_0 \| (100)$, T = 90°K, with lines from shell I to VIII. ν_{ESR} = 9.5 GHz (after Seidel (2)).

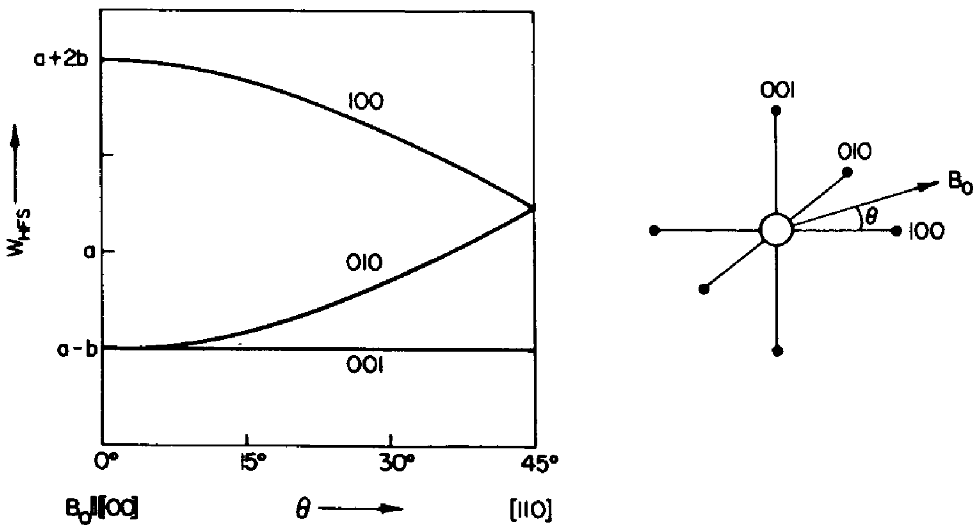

Fig. 5 Schematic representation of the angular dependence of the shf interaction of first shell nuclei in F centres. B_0 is rotated in a (001) plane.(after Seidel(2))

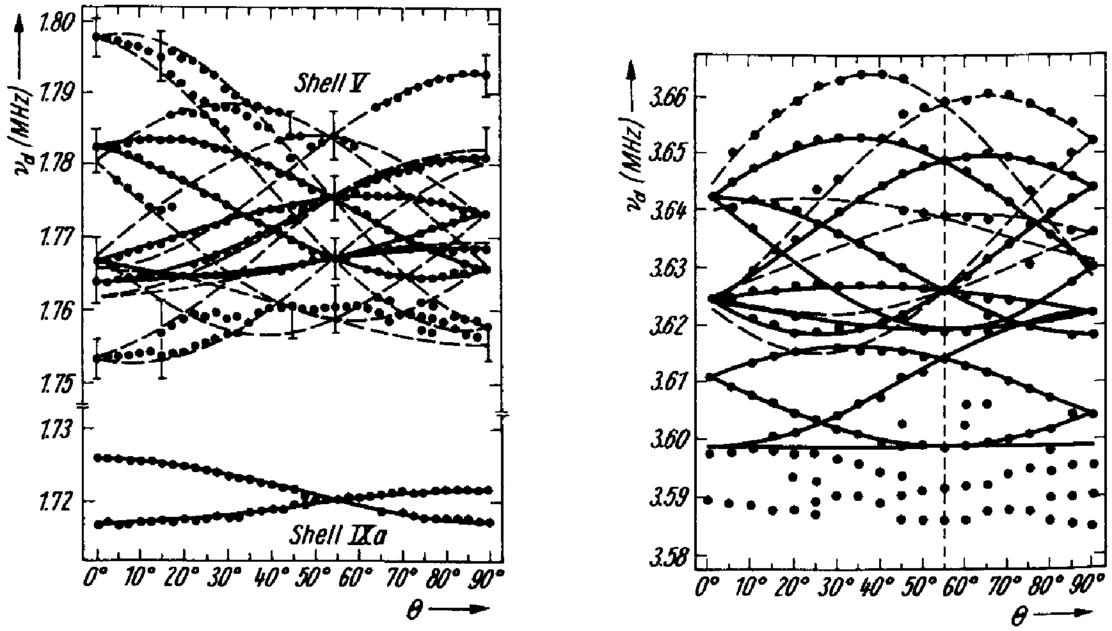

Fig. 6 Angular dependence of higher shell ν^{-}_{ENDOR} lines for F centres in KCl for B_0 rotated in a (110) plane. $\theta = 0^{o} \hat{=} (001)$. ν_{ESR} = 24 GHz, T = 77°K. Right side: upper curves belong to shell VI and lower curves belong to shell VIII.

3.3. Electronic Structure

According to Equ.(2) and (3) the shf interaction constants furnish an extraordinarily exact determination of the wave function $\psi(r)$ of the unpaired electron in its ground state. The isotropic shf constant is a direct measure of the density at the various sites of neighbour nuclei. For a theoretical interpretation of the results one has thus to discuss the electronic wave function of the unpaired electron. If one wants to do this from first principles this is quite a formidable task, which involves very difficult questions of molecular and solid state quantum theory, which cannot be discussed here. However, this theoretical part of the investigations is of great importance since the ENDOR measurements provide so much detailed information that a very good test of any theoretical model can be made.

In many ionic crystals the experimental results of vacancy centres are discussed in some form of a pseudopotential theory. In its simplest form a smoothly varying, vacancy-centred envelope function ψ_F is determined as a one-electron solution of an appropriate Schrödinger equation employing the potential of the centre and a simplified potential of the lattice where the detailed structure of the ions is neglected. This envelope function is then orthogonalised to the core wave functions ψ_i of the neighbour ions. (7,18,21,22,23,25). The centre wave function thus obtained is:

$$\psi = N \left(\psi_F - \sum_i \langle\psi_F|\psi_i\rangle \psi_i\right) \qquad (16)$$

N is a normalisation constant which generally is practically equal to 1.

In this "method of orthogonalised wave function" the centre electron is described by the one particle wave function ψ which is then used to calculate the interaction parameters according to Equ.(2) and (3).

The agreement between experiment and theory in the alkali halides obtained with this type of calculations is reasonably good for the first two or three shells of neighbour nuclei. The agreement for the isotropic shf constants for higher shell nuclei is still rather poor, the discrepancies being about two orders of magnitude for shells VIII and XI (5,9).

The theoretical interpretation of the quadrupole interaction is still more difficult. The main problems arise in connection with the proper treatment of the Sternheimer antishielding. For F centres in KCl the quadrupole interactions were discussed in detail in connection with the lattice distortion around the vacancy (26).

4. VACANCY CENTRES IN CRYSTALS WITH IMPURITIES

In many ionic crystals perturbed F-type centres can be produced if the crystals contain impurity cations. For example, if one bleaches optically at room temperature F-centres in potassium chloride containing Li^+ or Na^+ ions, perturbed F-centres are produced which are called F_A centres. As revealed by an ENDOR investigation, F_A centres are F centres where one of the 6nearest K-cations is replaced by Li^+ or Na^+. Fig. 7 shows the ENDOR spectrum for randomly oriented F_A(Li) centres in KCl for $B_o || (100)$ (27).

The spectrum shows clearly the ENDOR lines of the Li-impurity. The line denoted by $Li_{\parallel}$ is due to those Li nuclei parallel to the field direction, that denoted by $Li_{\perp}$ due to those perpendicular to B_o. The potassium lines appear in two groups that are slightly shifted with respect to each other. This is because in the F_A centre the four K nuclei in the symmetry plane perpendicular to the centre axis, which is the connection line between the vacancy and the Li^+ neighbour, are no longer equivalent. The ESR spectrum of the F_A centres differ only in the line width from that of the F centre (28).

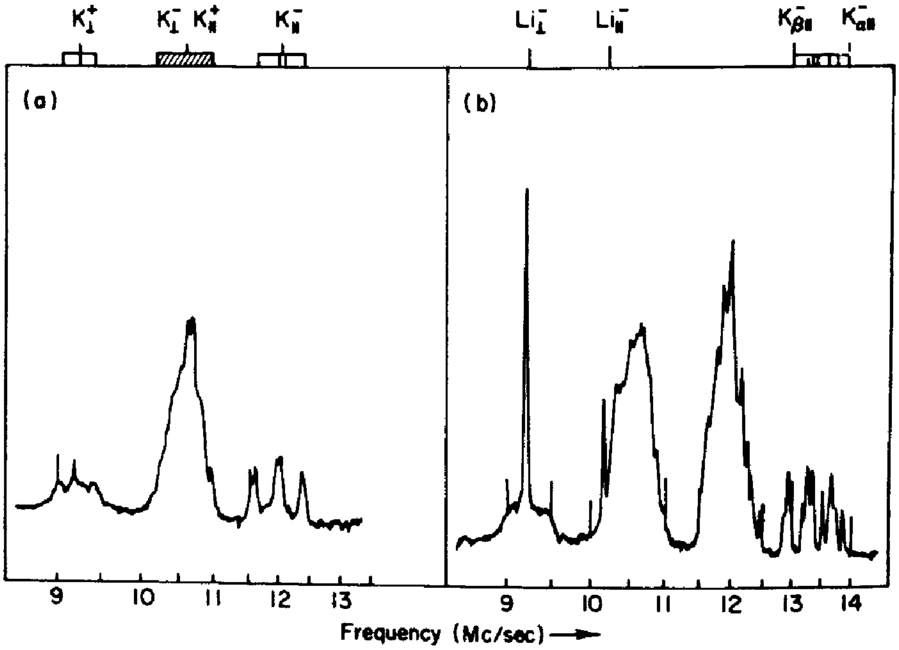

Fig. 7 ENDOR lines of first shell nuclei of F and F_A centres in KCl: Li, $B_o || (100)$, T = 90°K, ν_{ESR} = 9.38 GHz.
a) F centres in the quenched crystal
b) F_A centres after five minutes irradiation by 5460 Å light at room temperature. (after Mieher (27)).

Magnetic resonance studies of Z centres in alkali halides, which are formed in crystals with divalent cation impurities, were less successful. For instance as a result of the ENDOR investigation of Z_1 centres the atomic structure of the Z_1 centres could not be established unambiguously. Only two possible configurations could be given. Very many ENDOR lines could be measured, but a complete analysis could not be achieved (29).

Another interesting example of a perturbed F centre in an alkali halide is the H_2O^--centre in KCl. It is produced photochemically from OH^--centres. The ESR-spectrum is very similar to that of the F centre. In the ENDOR spectrum below 15°K ENDOR lines from protons can clearly be seen. From the analysis the model shown in Fig.8 could be derived: a H_2O molecule occupies an F centre with its C_{2v} molecular axis along a $\{111\}$ direction. The shf interactions with the nearest lattice neighbours are very similar to those of the F centres. Therefore the centre was sometimes called the "wet F centre". (30).

5. F AGGREGATE CENTRES

When F centres in alkali halides are exposed to light in the F-band at room temperature aggregation of F centres occurs. Part of the F centres form aggregate centres such as M and R centres, others form loose aggregates. The F centres in the loose aggregates are somewhat perturbed. Their ESR linewidth is decreased compared to normal F centres, the line shape altered in the central part of the ESR line, and the relaxation times are shorter (5,31). The ENDOR spectrum, however, shows no difference from the unperturbed F centre. (31). The changes in the ESR spectra are explained as due

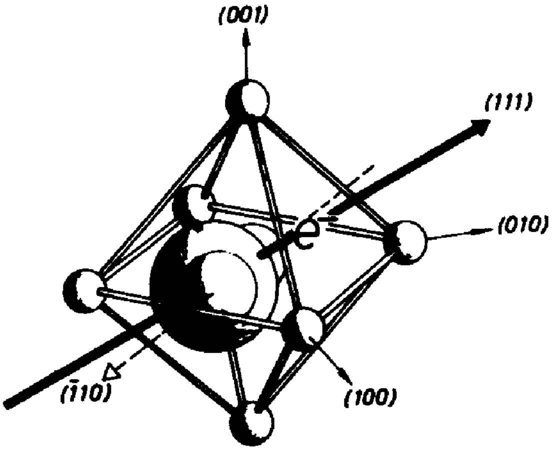

Fig. 8 Model of the H_2O^--centre in KCl. (after Rusch (30)).

to exchange effects between loosely aggregated F centres (31).

M centres have a diamagnetic ground state (32) and the ESR of R centres can only be observed under special conditions (33). The models for the M and R centre in KCl are shown in Fig.9.

They were definitively confirmed through the ESR and ENDOR measurements in their metastable multiplet states with lifetimes of many seconds into which they can be brought optically (34,35).

Their electronic states can be described in a very good approximation as Heitler-London combinations of two respectively three F centre wave functions. For the M centre triplet state in KCl this is immediately seen in the ENDOR spectrum of the nearest neighbouring nuclei shown in Fig.10.

New lines appear with the M excitation. The lines in the range of 18 to 21 MHz are due to the K^{I}_{α} nuclei (see Fig.9) and have approximately twice the frequency of the corresponding F centre K^{I} lines. The electron density of K^{I}_{α} is approximately twice the value of the F centre due to the two M centre electrons. (34).

For magnetic resonance investigation of multiplet states of M centres in the alkaline earth fluorides the reader is referred to (8).

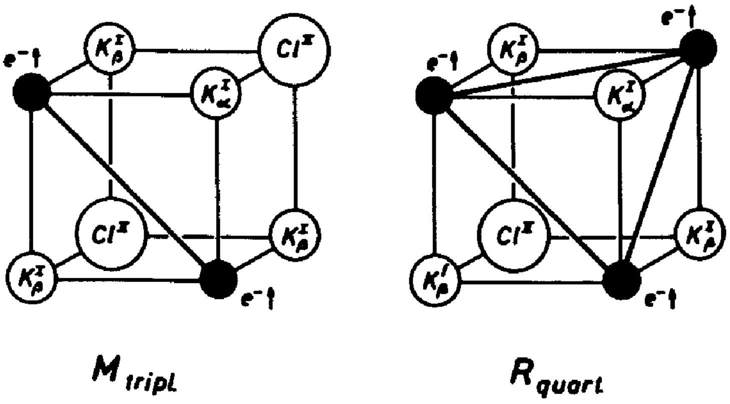

Fig. 9 M and R centre in KCl. Spin configurations are shown for the metastable multiplet states. (after Seidel (36)).

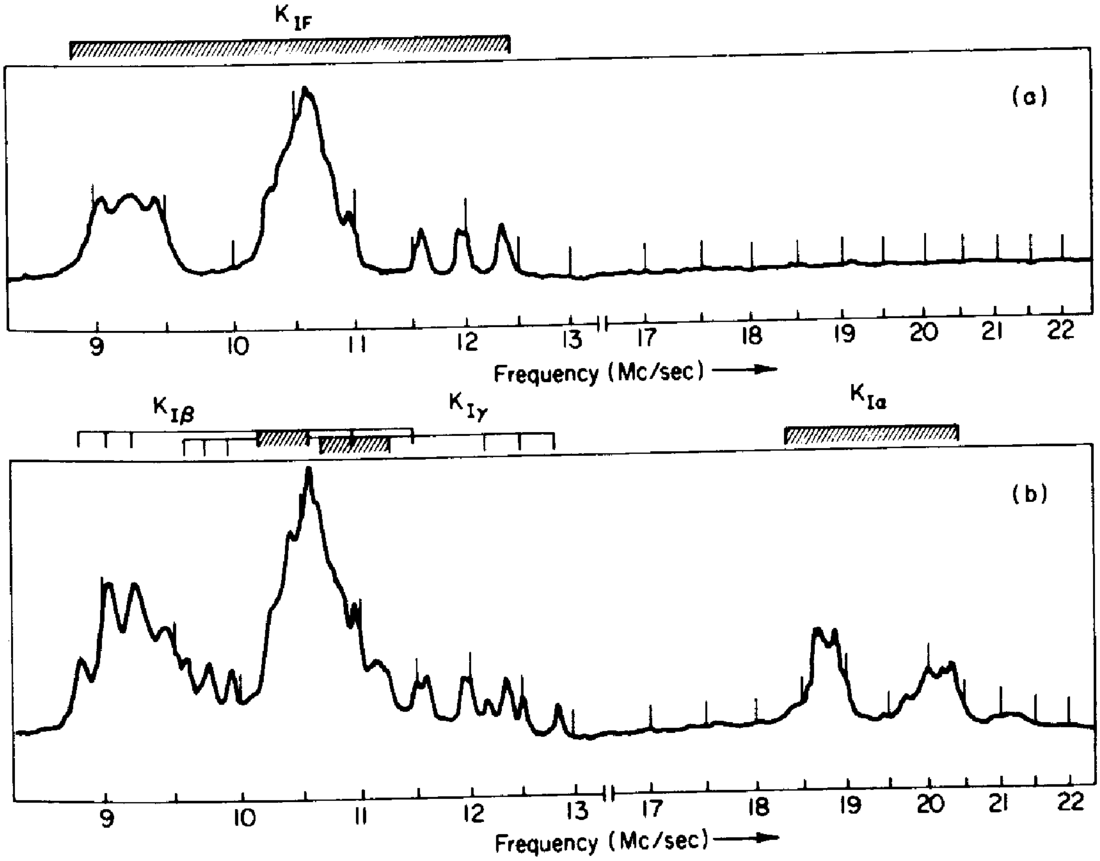

Fig. 10 ENDOR spectra of F and M centres in KCl. $B_o || (100)$, $T = 90^oK$, $\nu_{ESR} = 9.38$ GHz.

a) without illumination (F centres, first shell)

b) during excitation with 3650 Å. M centres in the triplet state (after Seidel (34)).

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