ENDOR STUDY OF HYDROGEN ATOMS IN KCl-CRYSTALS

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Résumé. — Des mesures d'E. S. R. ont montré l'existence d'atomes d'hydrogène neutre dans les sites interstitiels du réseau des halogénures alcalins à basse température. Ces centres d'hydrogène sont appelés « Centres U_2 ». Les interactions hyperfines avec le proton et les quatre noyaux d'halogène plus proches voisins sont résolues dans le spectre E. S. R. Pour résoudre les interactions hyperfines et celles de quadrupoles avec les autres noyaux du réseau environnant, on a effectué des mesures E. N. D. O. R. sur les centres U_2 dans KCl à 77 °K. L'analyse des spectres E. N. D. O. R. a donné des valeurs précises pour les constantes d'interactions hyperfines et de quadrupole des atomes K et Cl plus proches voisins. La constante hyperfine isotrope des Cl plus proches voisins est 24 fois plus grande que celle des K, bien que les deux noyaux soient sur des positions de première couche équivalentes. L'interaction hyperfine avec les deux couches suivantes de chlore et la couche suivante de potassium a pu être résolue. La constante hyperfine isotrope des noyaux de potassium de la seconde couche a été trouvée plus grande qu'on ne s'y attendait. En orthogonalisant la fonction d'onde 1 S de l'hydrogène pour les noyaux des ions voisins, et en tenant compte du recouvrement mutuel des ions K^+ et Cl^- voisins, on a évalué théoriquement les constantes d'interaction hyperfine et de quadrupole.

Abstract. — E. S. R. measurements had given evidence for the existence of neutral hydrogen atoms in interstitial lattice sites in alkali-halides at low temperatures. These hydrogen centers are called U_2-centers. The hyperfine interactions with the proton and with the four nearest halogen nuclei are resolved in the E. S. R. spectrum. In order to resolve hyperfine and quadrupole interactions with further nuclei of the surrounding lattice E. N. D. O. R. measurements have been performed on U_2-centers in KCl at 77 °K. The analysis of the E. N. D. O. R. spectra gave precise values for the hyperfine and quadrupole interaction constants of the next nearest neighbour chlorine and potassium nuclei. The isotropic hyperfine constant of the next nearest chlorine neighbours is 24 times larger than that of the next nearest potassium neighbours, although both nuclei are on equivalent first shell positions. The hyperfine interaction with two further chlorine and one further potassium shells could be resolved. The isotropic hyperfine constant of the second shell potassium nuclei is found to be unexpectedly large. A theoretical estimate of the hyperfine and quadrupole interaction constants was made by orthogonalizing the 1 S hydrogen wave function to the cores of the surrounding ions and by taking into account the mutual overlap of neighbouring potassium and chlorine ions.

I. **Introduction.** — Colour centres containing hydrogen in a variety of host lattices have found an increasing interest over the last years. Due to the small mass and simple electronic structure of hydrogen these centres can be considered as model point defects for the study of various more complicated solid state phenomena. The fact, that hydrogen can be incorporated charged as H^- and neutral H^0 in various lattice sites, enables the application of several techniques of investigation. In the alkalihalides all the hydrogen centres possess absorption bands in the ultraviolet and are therefore called U-centres. So far one knows two centres with neutral hydrogen atoms in alkalihalides, one of which has been known for many years and is called the U_2-centre. Since neutral hydrogen atoms are paramagnetic one can use apart from optical methods also Electron Spin Resonance (E. S. R.) and as you will see Electron Nuclear Double Resonance (E. N. D. O. R.) for its investigation. With these latter techniques one can obtain a detailed knowledge of the atomistic structure of the U_2-centre and precise values of the electron density of the ground state centre wave function at the proton and various sites of neighbouring lattice nuclei.

The subject of my talk is to report on an E. N. D. O. R. investigation of U_2-centres in KCl. Let us first have a look at the E. S. R. spectrum of U_2-centres (Fig. 1).

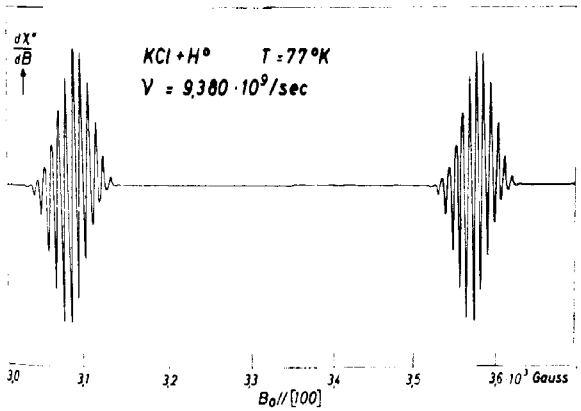


FIG. 1. — E. S. R.-spectrum of the U_2-centre at 77 °K. $B_0 \parallel [100]$.

As usual the first derivative of the resonance curve is recorded versus the magnetic field. The field is oriented along a [100] crystal axis. You see two line groups separated by about 500 G, each of which consists of 13 equidistant lines, which are nearly resolved. The resonance was measured at 77 °K, because U_2-centres are stable only at low temperatures. They were produced by photodecomposition of OH^- or SH^- centres at 77 °K.

This spectrum was first recorded by Sander some four years ago and he concluded from it that the hydrogen atom is in an interstitial position.

In figure 2 you see the interstitial hydrogen atom

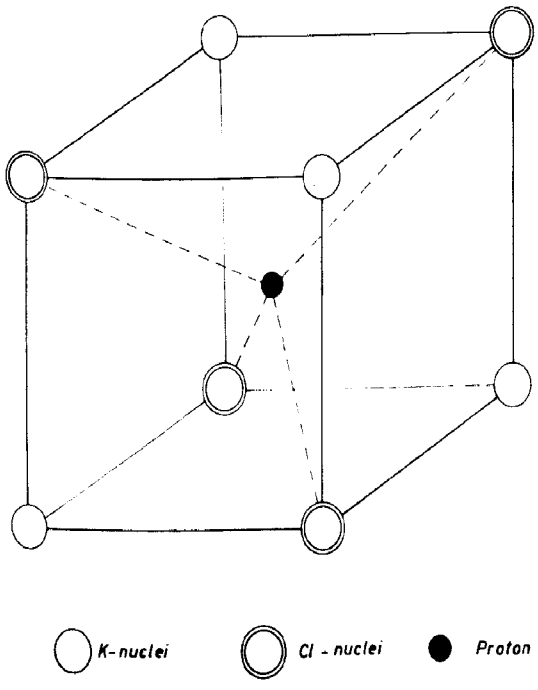


FIG. 2. — Model of the U_2-centre.

surrounded by 4 Cl and 4 K ions, which both have the same distance from the H atom. The resonance spectrum is explained as follows : the unpaired electron spin at the H atom interacts with the proton nuclear magnetic moment. Since the proton nuclear spin $I_p = 1/2$, one obtains two E. S. R.-lines, the separation of which is given by the proton hyperfine interaction. In fact, the separation is about 3 % less than it would be for the free atom. The additional splitting into 13 lines is explained by an interaction with 4 equivalent nuclei of spin 3/2. The total nuclear spin would be $4.3/2 = 6$, giving magnetic quantum numbers ± 6, ± 5, ± 4..., 0, thus 13 lines with the observed relative intensity ratio. A comparison of the splittings in NaCl, KCl and KBr – Na and Br have different nuclear moments and hence should give different splittings – showed, that the interaction occurs with the 4 halogene nuclei, that is here the Cl nuclei. One estimates from the spectrum that the interaction with the potassium nuclei could be atmost 10 % of that with the Cl nuclei.

These results formed the starting point for our investigation. The question was, why the hyperfine (hf) interaction with the Cl neighbours should be so much bigger than that with the K nuclei. (For the sake of simplicity we denote this interaction simply by hyperfine interaction and not by superhyperfine interaction, as it is often done.) If one assumes that the unpaired spin distribution is completely outside the K^+ and Cl^- ion cores, one would expect the ratio of the hf-constants of the Cl and K neighbours to be that of the nuclear moments, namely 2. If some unpaired spin density moves within the ion cores, however, their structure will influence the hf-interaction considerably. An estimate of the influence of the n. n. K^+ and Cl^- ions was made by Mimura and Uemura assuming that the wavefunction of the U_2-centre is the 1 s hydrogen function. It yielded a value of only 4 for the ratio of the hf-constants. In view of this discrepancy it was desirable to measure accurately the hf-interactions with the n. n. Cl and K nuclei and possibly with further nuclei of the surrounding lattice in order to get more detailed information about the groundstate wave function of the U_2-centre.

E. S. R. is not able to resolve hf-interactions of the n. n. K nuclei. With the E. N. D. O. R. method, however, one can obtain a much higher resolution and not only resolve the interactions with the n. n. K nuclei but also with nuclei of the further lattice surroundings.

II. Brief description of the E. N. D. O. R. method. — In order to explain the E. N. D. O. R. measurements it is convenient to consider first the energy levels of the U_2-centre. For the sake of clear-

ness the energy level scheme is very much simplified, that is, we consider only the system Electron + Proton + one Cl neighbour nucleus.

In figure 3 we have indicated at the left side the Electron-Zeeman splitting. Each Zeeman level is split into two sublevels because of the hf-interaction with the proton. The further hf-interaction with the Cl nucleus splits each proton sublevel into 4 Cl sublevels since the Cl nuclear spin is 3/2. Both the Cl and K nuclei have an electrical quadrupole moment. Thus in an electrical field gradient these levels are shifted somewhat what is indicated at the right side of figure 3.

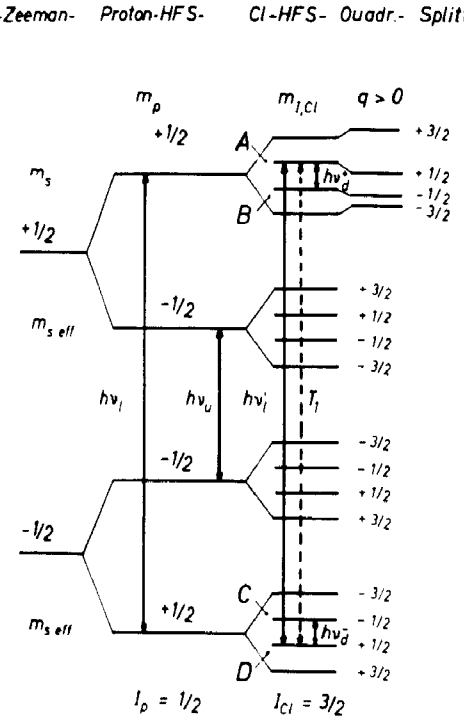


FIG. 3. — Energy levels of the system Electron + Proton + Cl-neighbour nucleus.

The complete Spin-Hamiltonian of the U_2-centre reads as follows :

$$\mathcal{H} = g_e \mu_B \mathbf{B}_0 \mathbf{S} - g_p \mu_K \mathbf{B}_0 \mathbf{I}_p + a_p \mathbf{I}_p \mathbf{S} + \\ + \sum_k (\mathbf{I}_k \tilde{A}_k \mathbf{S} + \mathbf{I}_k \tilde{Q}_k \mathbf{I}_k - g_{I,k} \mu_K \mathbf{B}_0 \mathbf{I}_k) . \quad (1)$$

The sum runs over all nuclei of the lattice which interact with the unpaired electron. In the energy level diagram we can visualize the different electron magnetic and nuclear magnetic resonance transitions. The transitions $h\nu_l$ and $h\nu_u$ correspond to the centres of the two E. S. R. line groups ($\Delta m_s = \pm 1$, $\Delta m_p = 0$), $h\nu_{l'}$ would correspond to one of the resolved E. S. R. lines, if one neglects the fact, that we have in reality 4 equivalent Cl nuclei. In the stationary E. N. D. O. R. experiment, as it was developed by Seidel and which we have applied, one induces nuclear magnetic transitions between hyperfine levels by applying an additional radio frequency field, and one observes these transitions through a change of the saturated electron resonance signal. Let me explain this in more detail : we consider the levels A and D. Without application of a microwave field the population of the levels obeys the Boltzmann distribution. On applying a microwave field, one diminishes the Boltzmann population difference, which is given by the energy difference between the levels ; at a high microwave power one may be able to equalize the populations of A and D, provided the spin lattice relaxation time is not too short. The resonance transition is then saturated, in the extreme case one cannot observe a microwave absorption any more. It is important to note, that for instance the level B is not affected by the saturation. If one now induces simultaneously a nuclear magnetic resonance transition connecting for instance the levels A and B ($h\nu_d^+$), one reduces the population of the level A, the levels A and D are not any more equally populated, so that the saturation of the electron resonance transition is reduced, the resonance signal increases again. Or, in other words, the E. N. D. O. R. transitions cause the spin lattice relaxation time to be shortened through providing relaxation shunts (there will be a relaxation between B and D), so that for a given microwave power with a now shorter effective relaxation time the saturation is reduced, the signal enhanced. So in the E. N. D. O. R. method one records the desaturation of the E. S. R. signal which acts as an indicator for the N. M. R. transitions of nuclei, which are coupled to the electron.

The N. M. R. transitions could be not observed directly in a straight N. M. R. experiment because of the low concentration of the paramagnetic centres. The fact, that they are detected through E. S. R., however, implies an energy amplification through « quantum transformation » by the ratio of the E. S. R. and N. M. R. transition energies which is roughly given by the ratio of the electron magnetic and nuclear magnetic moments, that is of the order of 10^3 to 10^4. In addition, the population difference between the nuclear levels is enhanced through the E. S. R. saturation (« pumping »), which results in a further amplification.

So far we have not seen, why in an E. N. D. O. R. experiment the resolution is so much higher than in an E. S. R. experiment. Suppose, the width of all the levels would be the same and would be given by the life time or say by the spin lattice relaxation time. Then the linewidths of the E. S. R., N. M. R. and E. N. D. O. R. lines would all be equal and E. N. D. O. R. would not

yield a higher resolution than the ordinary E. S. R. experiment. If the unpaired electron experiences hf-interactions with lattice nuclei, however, the E. S. R. line is inhomogeneously broadened, that is, its width is given mainly by the distribution of the local field seen by the electron and not by the spin lattice relaxation. The local field thereby is given by a superposition of the externally applied dc field and all dipole fields of the neighbouring lattice nuclei. The local field varies practically continuously in a certain range around B_0. The linewidth of the E. S. R. lines can then be characterised by

$$\Delta\nu_e = \frac{g_e \mu_B}{h} \Delta B_0$$

In order to point out the main feature let us assume, that the local field at the neighbouring nucleus be the same — this is not quite true but sufficiently to see the order of magnitude effect. Then

$$\Delta\nu_d = \frac{g_I \mu_K}{h} \Delta B_0 .$$

With prevailing inhomogeneous broadening the gain in resolution if one observes N. M. R. or E. N. D. O. R. transitions, is then given by

$$\frac{\Delta\nu_e}{\Delta\nu_d} = \frac{g_e \mu_B}{g_I \mu_K}$$

and of the order of 10^3 to 10^4.

The frequency of the additionally applied radio frequency field, which induces the E. N. D. O. R. transitions, yields us the desired information about the hf-constants.

It is given by

$$\nu^{\pm} = \left| \frac{1}{2h}(a_k + b_k(3\cos^2\alpha_k - 1)) \mp \nu_k + \right.$$
$$\left. + \frac{3}{h} q_k(3\cos^2\beta_k - 1)(m_I - \tfrac{1}{2}) \right| . \quad (2)$$

This is a first order perturbation solution of the Spin - Hamiltonian with $\Delta m_s = 0$, $\Delta m_I = \pm 1$, $m_I = 3/2, 1/2, -1/2$.

a_k is the isotropic part of the hf-tensor, b_k the anisotropic part, q_k is the quadrupole interaction constant. α_k is the angle between the principal axis of the hf tensor and the field direction, β_k is the angle between the principal axis of the quadrupole tensor and the field direction (we have assumed axial symmetry here, which is correct for the n. n. neighbours). For the experiment this angular dependence of the E. N. D. O. R. frequencies is very important : one measures the E. N. D. O. R. frequencies as a function of the crystal orientation with respect to the magnetic field. From the angular dependence one then determines the hf- and quadrupole-constants and the orientation of the hf-and quadrupole-tensors.

For each nucleus there are always two E. N. D. O. R. frequencies which differ by twice the Larmor frequency ν_k of the free nucleus. a_k, the isotropic hf constant, contains the information about the density of the unpaired electron at the nuclear site k

$$a_k \propto |\psi(k)|^2 .$$

So much for a brief outline of the E. N. D. O. R. method.

III. **Results for the U_2-centre.** — In figure 4 you

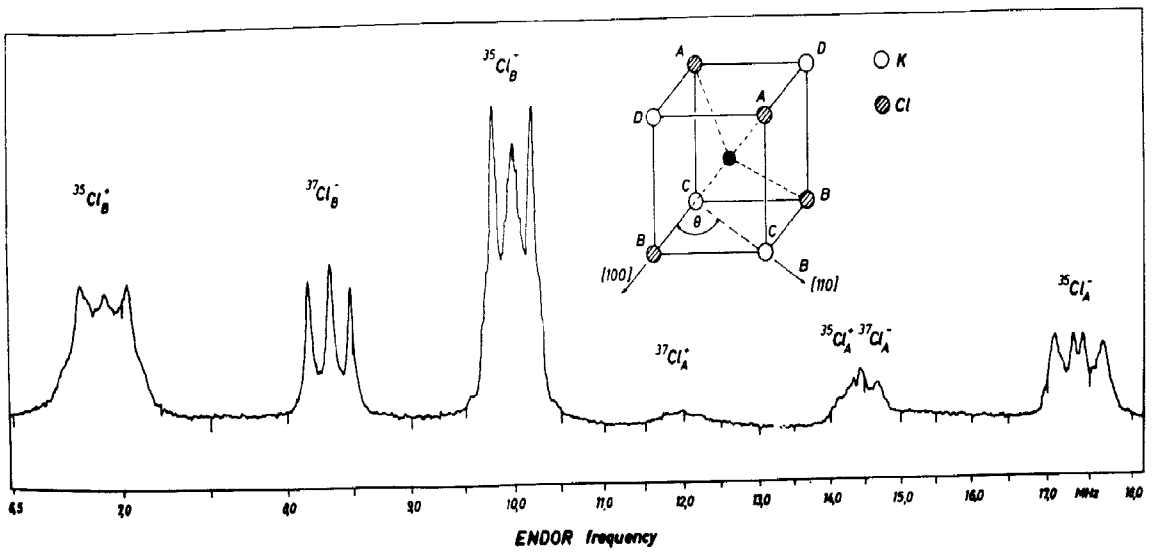


FIG. 4. — E. N. D. O. R.-spectrum of the ^{35}Cl and ^{37}Cl n. n. nuclei. $B_0 \parallel [110]$ The middle line of the upper E. S. R.-linegroup was saturated. $T = 77$ °K, $\nu = 9\,320$ MHz.

see as an example the E. N. D. O. R. spectrum of the n. n. Cl nuclei. On the abscissa the E. N. D. O. R. frequencies are plotted, the lines represent the desaturation of the E. S. R. signal. The magnetic field is in the [110] direction, where always two of the four nuclei are equivalent (AA, BB), that is, they have the same angle α_k and β_k with respect to the magnetic field. One expects therefore two lines due to nuclei A and two lines due to nuclei B. It is characteristic for the chlorine E. N. D. O. R. lines, that they appear twice because of the two isotopes ^{35}Cl and ^{37}Cl, which have slightly different nuclear moments. ^{35}Cl has a somewhat larger moment, hence a higher E. N. D. O. R. frequency. The line intensity reflects the natural abundance of the two isotopes (75 % ^{35}Cl, 25 % ^{37}Cl). Furthermore each line is split into a triplet. This is due to the quadrupole interaction. As is shown in the energy level diagram (Fig. 3) the quadrupole interaction shifts the four equally spaced hf-levels, so that instead of one E. N. D. O. R. line there are three. The quadrupole splitting is also angular dependent. The angular dependence of the hf-interaction causes the whole line groups to shift if one rotates the crystal, the angular dependence of the quadrupole interaction varies the magnitude of the quadrupole splitting upon rotating the crystal.

The E. N. D. O. R. spectra of the U_2-centre are not described accurately enough by equation (2) which is a first order perturbation solution of the Spin Hamiltonian. It would only hold if all hf-terms were small compared with the electron Zeeman term and also it would be necessary for instance that the anisotropic part of the hf-interaction was small compared with the isotropic part of the interaction. This is not the case. One has to go to higher order perturbation treatment or solve $\mathcal{H}$ exactly. The exact solution describes all details of the E. N. D. O. R. spectra. An exact analysis of the spectra requires a great deal of computational work.

The results are compiled in table 1. You see that the isotropic hf-constant of the n. n. K nuclei is indeed very much smaller than that of the n. n. Cl nuclei : the ratio between them is about 24. The anisotropic part is in both cases rather large. Both nuclei show quadrupole interactions, that means that at the nuclear sites there is an electrical field gradient pointing to a lattic distortion around the hydrogen atom.

We could also resolve interactions with various nuclei which are further out in the lattice. Let us have a brief look at the further lattice surroundings of the U_2-centre (Fig. 5). You see the hydrogen atom with the four Cl and K neighbours of the first shell. The nuclei of a shell are characterized by the same distance from the proton. We could resolve the interactions with the nuclei of two more Cl shells and one more K shell.

I would like to draw your attention especially to the K nuclei of the second shell : these are those nuclei, which are immediate neighbours to the Cl nuclei of the first shell. We could analyse their interaction very accurately. The direction of the principal axis with the biggest interaction of the hf-tensor is indicated (Z_{HFS}),

TABLE 1

Hyperfine constants of the U_2-center in KCl in MHz (T = 77 °K)

nucleus	Distance in d = 1,57 Å	a/h	b/h	b'/h	$3q/h$	$3q'/h$	z_{HFS}	z_Q
^1H		1378.4						
$^{35}Cl^I$ ..	$1/2\sqrt{3}$	23,74	6.71	0	− 0.174	0	< 111 >	< 111 >
$^{39}K^I$ ...	$1/2\sqrt{3}$	0.983	0.457	0	+ 0.045	0	< 111 >	< 111 >
$^{35}Cl^{II}$.	$1/2\sqrt{11}$	~ 0.01	~ 0.05					
$^{39}K^{II}$ ..	$1/2\sqrt{11}$	0.123 ± 0.002	0.032 ± 0.002	0.010 ± 0.001	0.040 ± 0.002	~ 0	< 100 > − 2° (∓ 1°)	< 100 > + 15° (± 2°)
$^{35}Cl^{III}$.	$1/2\sqrt{19}$	0 ± 0.010	0.06 ± 0.01		0.025 ± 0.01		~ < 110 >	~ < 110 >

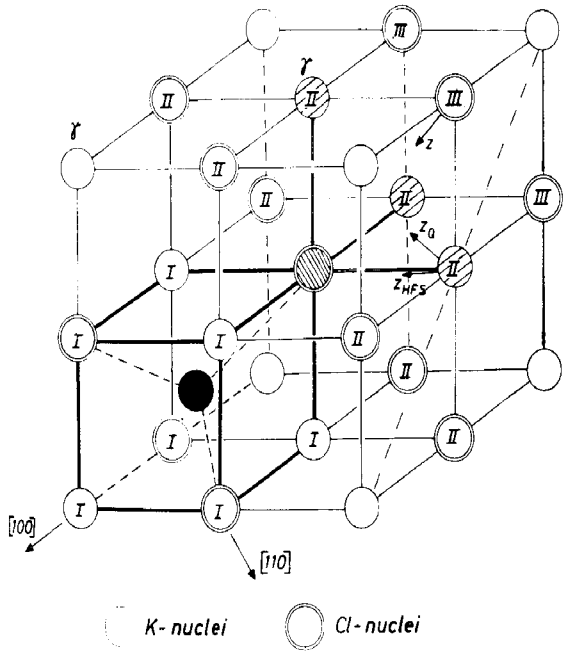


FIG. 5. — Extended lattice surroundings of the U_2-centre.

it nearly coincides with the connection line to the n. n. Cl-neighbour. The quadrupole principal axis (Z_Q) is displaced by about 16° with respect to Z_{HFS} in a (110) plane. The unexpected result is, that the isotropic constant $a(K^{II})$ is still very large — it amounts to 0,12 MHz. This is an order of magnitude more than for the Cl nuclei of the second or third shell. They show nearly only an anisotropic interaction.

Let us summarize the most important results yielded by the E. N. D. O. R. measurements : the E. N. D. O. R. analysis has confirmed beyond any doubt the model for the U_2-centre as an interstitial hydrogen atom. The hf-and quadrupole-interactions of the n. n. Cl and K nuclei could be determined very accurately and furthermore the interactions with two more Cl and one more K shell could be determined. The obtained hf-and quadrupole-constants are obtained through careful analysis of the spectra only and are thus purely experimental values. They are not based on special theoretical assumptions.

It is surprising that the ratio of the isotropic hf constants of the n. n. Cl to the n. n. K nuclei is so very large :

$$a^{Cl^I}/a^{K^I} = 24 .$$

This means – taking the magnitude of the nuclear moments into account – that the electron density at the Cl sites is 12 times as large as at the K sites. It is furthermore surprising, that the isotropic constant of the second shell K nuclei is still so large, $a(K^{II}) = 0.12$ MHz.

Assuming, that the wave function is centered mainly in the immediate vicinity of the proton, one would expect for the nuclei of the second and third shell only anisotropic interactions, what we have indeed observed for the Cl-nuclei of the outer shells.

IV. **On the theoretical interpretation of the results.** — In the remaining few minutes I would like to say a few words on the theoretical interpretation of the results. I will confine the discussion to the isotropic interaction of the first shell nuclei and the 2nd shell K nuclei, and leave out quadrupole and anisotropic interactions.

In order to understand quantitatively the observed interactions one should know the correct wave function for the U_2-centre. This wave function would be a very complicated many electron and many centre function. Even in the Hartree Fock approximation it is not possible today to solve the Schrödinger equation for the system hydrogen atom plus crystal with sufficient accuracy. One has therefore to try crude approximations, which can be justified afterwords to the extent to which they were succesful. In the case of the U_2-centre we can hope to be able to start off with the well known 1 s hydrogen function. The crudest thing one can do is to take as U_2-centre function only the hydrogen 1 s function. The calculated hf-constants with it, however, are three orders of magnitude smaller than the observed ones. Well, part of the hydrogen 1 s function will move within the cores of the neighbouring ions, so that a better approximation will be to take a Slater determinant containing the hydrogen 1 s function and the core orbitals of the neighbour ions. With this one fullfills at least the requirements of the Pauli principle. For the unpaired spin density this is equivalent to orthogonalising the hydrogen 1 s function to the cores of the neighbouring ions. Orthogonalising leads to admixtures of neigbour core orbitals into the hydrogen 1 s function (φ_H) in the following way :

$$\psi_{u_2} = N\left(\varphi_H - \sum_{i,\alpha} < \varphi_H \psi_i^\alpha > \psi_i^\alpha\right). \qquad (3)$$

The sum runs over all the filled orbitals (i) of the neighbour ions (α). The admixture coefficients are the overlap integrals. It is illustrating to write out ψ_{u_2} with the most important admixtures. One obtains as a wave function for the U_2-centre :

$$\psi_{u_2} = 1.09\left(\Phi_H - \sum_{\alpha=1}^{4}(0.07\,\psi_{3s}^{Cl_\alpha} - 0.17\,\psi_{3p}^{Cl_\alpha}) - \sum_{\beta=1}^{4}(0.04\,\psi_{3s}^{K_\beta} - 0.06\,\psi_{3p}^{K_\beta})\right). \qquad (4)$$

The *s*-admixtures yield the most important contributions to the isotropic constant because of the high *s*-density at the nuclear sites. For the calculation we have used the Hartree Fock functions of free ions. With this wave function we get the following theoretical hf-constants (table 2, last column) : we obtain the right order of magnitude, however the K^{I} value is too high, the ratio of the first shell isotropic constants is only 4. The value for K^{II} is too small by two orders of magnitude. Thus the simple orthogonalization cannot explain the results.

TABLE 2

Comparison of experimental and theoretical hyperfine constants (in MHz)

Nucleus	Constant	Experimental	Theoretical with ion overlap	Theoretical without ion overlap
$^{35}Cl^{I}$	a/h	23.74	17.2	18.9
	b/h	6.71	3.5	3.9
	$3\,q/h$	− 0.174	− 0.12	
$^{39}K^{I}$	a/h	0.983	1.65	4.55
	b/h	0.457	0.46	0.69
	$3\,q/h$	+ 0.045	+ 0.10	
$^{39}K^{II}$.....	a/h	0.123	0.080	8×10^{-4}
	b/h	0.032	0.030	0.026
	$3\,q/h$	0.040	$2{,}7 \times 10^{-3}$	
$^{35}Cl^{III}$ ...	a/h	0 ± 10^{-2}	2×10^{-2}	~ 0
	b/h	0.06 ± 0.01	0.030	0.024

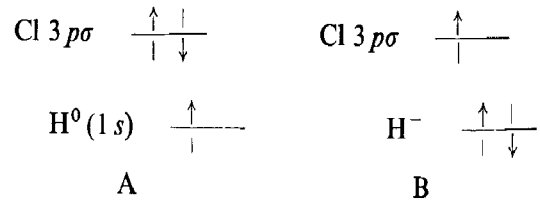
We have assumed so far in the orthogonalization procedure (which is actually the Schmidt-orthogonalization) that the core orbitals of neighbouring ions are mutually orthogonal. If one takes the Hartree-Fock functions of the free ions, this is not true. E. g the overlap integral

$$< Cl_{3p}\, K_{3p} > = 0.07$$

is of the same order as the admixture coefficients in ψ_{u_2}. In fact, if one takes the nonorthogonality of the core orbitals of neighbouring ions into account one can explain the order of magnitude of the observed isotropic hf-constants of the K nuclei in the second shell. Thus what happens is an electron transfer from the hydrogen 1 *s* through the core of the first shell Cl-ion to the second shell K nucleus.

If one takes the mutual ion overlap into account one kills two birds with one stone. It affects namely also the admixture of the first shell *K* function into φ_H via the combined overlap $< \varphi_H\, Cl^{I} > < Cl^{I}\, K^{I} >$. It works out to diminish the K^{I} admixtures. Of course, a similar effect holds for the Cl^{I} admixtures, however the relative change of the admixture is largest for the K nuclei because of the strong $< \varphi_H\, Cl^{I} >$ overlap.

In table 2, fourth column, you see the results with the mutual ion overlap taken into account. The value for K^{I} is strongly reduced, the ratio for the isotropic constant is now 10.4 : 1. Also you see that for $a^{K^{II}}$ we get the right order of magnitude. The wavefunction obtained through careful orthogonalization can thus explain a large ratio between the isotropic constants without any further assumptions. However, there remain still serious discrepancies. Amongst them, e. g., is the fact, that we observed a small positive g-shift whereas with such a function one would calculate a negative one, and furthermore, we have observed a proton-hf-constant which is 3 % less than the free atom value. The normalization factor is greater than 1 through the orthogonalization. Very recently three Japanese workers, Cho, Kamimura and Uemura (*J. Phys. Sol. Jap.* 1966, **21**, 2244) have suggested in order to improve this situation to assume a configuration mixing between the following configurations :



↑↓ symbolizes the filled 3 $p\sigma$ valence band. Configuration *A* consists of a filled 3 *p* band (or closed 3 *p* shell) and atomic hydrogen. Configuration B consists of a hole in the 3 *p* band and H^{-}. Because of the large Coulomb interaction between the two 1 *s* electrons the total energy of configuration B is larger than that of configuration *A*, however they are energetically close to each other so that B will mix into A through electron-electron interaction. This can be treated formally by introducing a mixing parameter μ between these two configurations. Treating this in a certain approximation (e. g. using free ion functions, taking unchanged 1 *s* orbitals in *B*) as the Japanese workers have done, this leads to the same expression for the unpaired spin density as if one introduced some covalent bonding between H_{1s} and $Cl_{3p\sigma}$. This introduces the mixing or bonding parameter in the following way into ψ_{Cl_2}

$$\psi_{Cl_2} = \frac{1}{1+\mu^2}\, 1.09 \times \times \left(\varphi_H - \sum_{\alpha=1}^{4} (0.07\, \psi_{3s}^{Cl_\alpha} - (\mu + 0.17)\, \psi_{3p}^{Cl_\alpha}) - \sum_{\beta=1}^{4} (0.04\, \psi_{3s}^{K_\beta} - 0.06\, \psi_{3p}^{K_\beta}) \right). \qquad (5)$$

The new normalization constant can become smaller than 1 now, what we need to explain the observed proton hf splitting. The Japanese workers have determined μ from the experimental proton hf-constant and then calculated the first shell hf-constants with this function, that is, assuming that the ion core orbitals are orthogonal. They obtain for the ratio $a^{Cl^{35}}/a^{K^{41}}$ only 3.4 and overestimate the positive g-shift by a factor of 5. Before judging this model further a calculation taking the mutual ion overlap into account will have to be carried out — as far as I know this is at present under way. One probably has to consider partial convalencies — whether or not they are so simple with one convalency parameter remains to be seen. But there are still other discrepancies I have not mentionned yet – we are still far from the correct wave function even for such a simple system.

Looking back at all the very precise experimental information which the analysis of the E. N. D. O. R. spectra has yielded and considering the difficulties one has with the current methods of the theoretical interpretation, I think one realises, that the E. N. D. O. R. measurements can reveal very subtle details of the interaction of such a simple impurity with the lattice. It seems that the theoretical approach to impurity centre wave functions will have to be improved greatly until we can understand the experimental results more quantitatively.

Bibliographie

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