ATOMIC HYDROGEN CENTRES IN IONIC CRYSTALS

J. M. SPAETH

Physikalisches Institut, Teilinstitut 2, Universität Stuttgart, 7 Stuttgart 1, Azenbergstrasse 12, FRG

Résumé. — Cet article est une revue des travaux expérimentaux et théoriques sur les centres de l'hydrogène atomique dans les halogénures alcalins et les fluorures d'alcalins-terreux. En raison de leur structure très simple, ces centres peuvent être considérés comme des modèles pour l'étude des propriétés des défauts ponctuels et leur interprétation théorique par des calculs basés sur les principes fondamentaux.

Abstract. — Experimental and theoretical work on atomic hydrogen centres in alkali halides and alkaline earth fluorides is reviewed. Because of their very simple structure these centres can be regarded as model systems for the study of the properties of point defects and their theoretical understanding by calculations from first principles.

From ESR and ENDOR spectroscopy the distribution of the unpaired hydrogen electron over several shells of neighbour ions was determined. The ground state wave function of the centre electron is highly localized. The present theoretical understanding of the structure of the ground state wave function is discussed with emphasis on interstitial centres in the alkali halides. Complete orthogonalisation of the ion wave function and some covalent charge transfer from the halogen ions to the hydrogen atom as well as the consideration of the hydrogen zero point vibrations are important features of the ground state. The results of optical absorption and magneto-optical measurements in the alkali halides are reviewed. The excited state is qualitatively understood to be not of the hydrogen type but to consist of the symmetry allowed linear combinations of the outer halogen p orbitals, whereby interactions between the halogen ions and their spin orbit interaction are to be considered. In alkali chlorides doped with some bromide or iodide interstitial hydrogen centres can be produced in a mixed configuration. Results of recent optical absorption and emission as well as ESR experiments are briefly described.

1. **Introduction.** — Impurity centres containing atomic hydrogen in ionic crystals have found considerable interest over the last decade of years. The reason for this is their particularly simple structure — a hydrogen atom on a substitutional or an interstitial lattice site. Especially for the study of structural aspects of point defects such as the electronic wave function for the ground state and excited states the hydrogen centres can be looked at as model systems. Calculations from first principles of a defect wave function represent a highly complicated many particle problem which could not yet be solved satisfactorily. Therefore the study of the simplest possible defects is desirable. The hydrogen atom is indeed the most simple impurity possible with its only one 1s electron. Also the free hydrogen 1s wave function should serve as a reasonably good starting wave function for the calculations of the interactions between the impurity atom and the surrounding lattice.

It will not be possible in this short article to review all the interesting work on hydrogen centres in all ionic crystals studied. I will restrict myself on alkali halides and alkaline earth fluorides and concentrate on those results which give characteristic information on the electronic structure of the centres. I will first review the spinresonance investigations of the ground state and their theoretical interpretation, then the optical work, and I will finally make a few remarks on some recent work in mixed alkali halides done in our Stuttgart group.

2. **Electronic structure of the ground state.** — 2.1 EXPERIMENTAL RESULTS. — The discussion of the interstitial centres will form the major part of this review. Figure 1 shows the atomistic models for the interstitial hydrogen centres in alkaline earth halides and alkali halides. In the alkaline earth halides the hydrogen atom is located in the body centre of a

cube of 8 halide ions, e. g. F^-, which all have the same distance from the hydrogen. Every second body

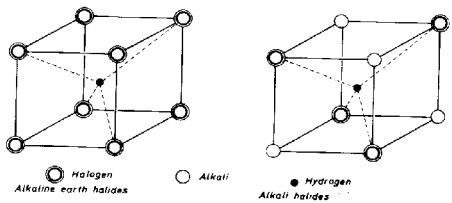


FIG. 1. — Model of the interstitial hydrogen centre in the alkaline earth halides and the alkali halides.

centre position is taken by a doubly charged alkaline earth ion. These centres can be produced by X-raying crystals containing H^- ions on halide sites at room temperature [1]. In the alkali halides the hydrogen atom is located at a similar interstitial position, however it is surrounded tetrahedrally by 4 halide ions and by 4 alkali ions. This difference is very important for the electronic structure of the centres : in the alkaline earth halides the centre electron sees in all 8 cube corners always the same diamagnetic halide ion cores whereas in the alkali halides it sees 4 halogen ion cores and 4 alkali ion cores which are adjacent and may be very different in size. In most alkali halides the cores of the negatively charged halogen ions are larger than the cores of the positively charged alkali ions. This — in a sense — is responsible for the fact that in the alkali halides the centre electron distribution is rather anisotropic, as will be shown below. The centres in the alkali halides can be produced by photodecomposition of OH^- or SH^- centres at temperatures below about 80 K [2-5].

Figure 2 shows the ESR spectrum for interstitial centres in CaF_2 taken from the work of Hall and Schumacher [1]. One can clearly see two line groups. The large splitting of about 520 G is due to the hyperfine interaction between the unpaired 1s centre electron and the proton, the two line groups correspond to the two possible orientations of the proton spin. The size of the splitting is characteristic for atomic hydrogen, it is only about 3 % larger than in the free atom. The additional well resolved structure of 9 equidistant lines with a characteristic intensity ratio (1 : 8 : 28 : 56 : 70 : 56 : 28 : 8 : 1) is due to the superhyperfine (shf) interaction with the 8 nearest F neighbour nuclei which for B_0 parallel to [100] are all magnetically equivalent. (Since ^{19}F has nuclear spin $I = \frac{1}{2}\,\hbar$, the total spin is 4 $\hbar$, hence 9 superhyperfine lines.) The doublet lines with small intensity between the F shf lines are due to forbidden transitions. The splitting between the F shf lines is essentially due to the isotropic shf constant or Fermi contact term and thus directly proportional to the density of the unpaired spin at the site of the nearest F nuclei. The isotropic shf constant of nucleus l is given by :

$$a_l = \tfrac{2}{3}\,\mu_0\, g_l\, \mu_K\, g_e\, \mu_B\, |\psi(r_l)|^2 \qquad (1)$$

$\psi(r_l)$ is the centre electron wave function at the site of nucleus l (g_e = electron g factor, g_l = nuclear g factor, μ_B = Bohr magneton, μ_K nuclear magneton). Thus this shf splitting gives the desired information about the ground state wave function.

Figure 3 shows the ESR spectrum of the interstitial centre in KCl, which was first measured by Delbecq, Smaller and Yuster [2] and with higher resolution by Sander [3]. Again one sees the characteristic proton hyperfine splitting. Here the interaction is about 3 % smaller than in the free hydrogen atom. Figuratively speaking, here the lattice draws some electron density away from the proton into the lattice, whereas it compresses the electron somewhat onto the proton in all alkaline earth fluorides and also the alkali fluorides. The splitting into 13 equidistant shf lines of each proton line is due to the shf interactions with the 4 nearest Cl neighbours. There is no shf interaction resolved with the 4 nearest K neighbours — their shf interaction is obviously much smaller.

The shf interactions with all nearest neighbours and several shells of neighbours in the further lattice surroundings were resolved by ENDOR experiments.

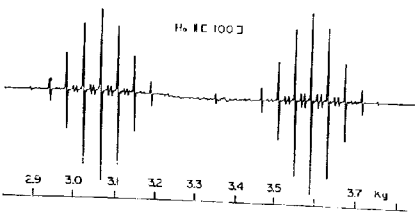


FIG. 2. — ESR spectrum of interstitial hydrogen centres in CaF_2. After Hall and Schumacher [1].

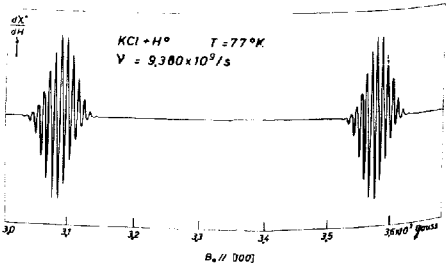


FIG. 3. — ESR spectrum of interstitial hydrogen centres in KCl. B_0//[100], T = 77 K.

In CaF_2 Hall and Schumacher [1] and more recently in SrF_2 Böttcher *et al.* [6] observed altogether 3 shells of F neighbour nuclei. Figure 4 shows the position of the 3 shells for CaF_2. The unpaired spin density at the second shell neighbours in CaF_2 is only about 0.5 % of that at the first shell. In the third shell it is only 0.02 %, that is almost vanishing. The axes of the shf tensors coincide with the connection lines between the proton and the respective F nuclei. The results in SrF_2 are very similar, the absolute values being some 20 % smaller because of the bigger lattice constant. These results show qualitatively, that the wave function of the centre electron is highly localised within the first shell.

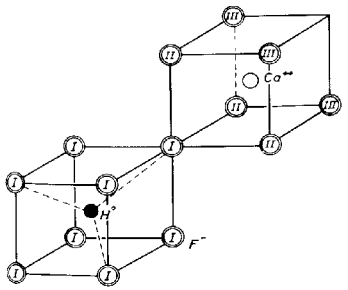


FIG. 4. — Interstitial hydrogen centres in CaF_2 : lattice positions of higher shell neighbours.

In many alkali halides ENDOR experiments were performed in our Stuttgart group [7-10]. Figure 5 shows the positions of higher shell nuclei with respect to the hydrogen atom. Shf interactions could be resolved with first shell alkali and halogen neighbours, second shell alkali and halogen and third shell halogen neighbours. It is characteristic for the results that the unpaired spin density at the first shell alkali neighbours is indeed very low and that the alkali nuclei of the second shell show still a rather large unpaired spin density, whereas the second shell halogen nuclei have only the classical dipole-dipole interaction. The principal axis of the second shell alkali shf tensor points nearly to the first shell halogen indicating that a transfer of unpaired spin density from the hydrogen atom via the halogen ion core to the second shell alkali ion is responsible for the observed spin density out there.

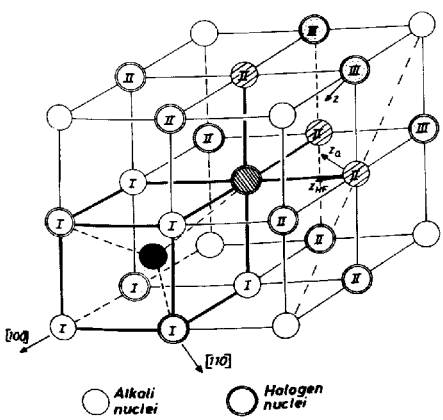


FIG. 5. — Interstitial hydrogen centres in alkali halides : lattice positions of higher shell neighbours.

In the alkaline earth fluorides the isotropic F shf interaction drops by roughly a factor of two on going from CaF_2 to BaF_2, and very similarly a drop by a factor of 2 is observed for the isotropic Cl shf interaction on going from NaCl to RbCl. This can qualitatively be understood by considering that the lattice constant increases from CaF_2 to BaF_2 and NaCl to RbCl, respectively, and therefore there is decreasing overlap between the hydrogen atom and the F^- and Cl^- ion cores, respectively. However the changes in the isotropic shf constants for the nearest K nuclei in the row of potassium halides from KF to KI are much more dramatic although the total change of the lattice constant is similar to that in the chloride or fluoride row. Table I shows the results for the isotropic K shf constants a. On going from KF to KCl a of the nearest K neighbours ($a(K^I)$) drops by nearly an order of magnitude, again so on going further to KBr. A recent result (M. Wagner and J. M. Spaeth, 1973, to be published) for KI, however, shows an increase of the isotropic constant compared to KBr although the lattice constant is still larger in KI, thus K^I further away from the proton. Looking at $a(K^{II})$ of those second shell K nuclei which are immediate neighbours to the first shell halogens one finds in KCl some 10 % compared to the first shell K nuclei which seems a reasonable order of magnitude for a weak transfer effect through the halogen core. This value increases only slightly on going to heavier

TABLE I

Isotropic K shf *constants of* H_i^0 *centres in alkali halides* (*in* MHz)

	a (K^I)	a (K^{II})	d [Å]
KF	7.54	—	2.66
KCl	0.983	0.123	3.14
KBr	0.113	0.160	3.30
KI (*)	0.656	0.163	3.52

d = nearest neighbour distance. Data after M. Sturm and J. M. Spaeth [10].

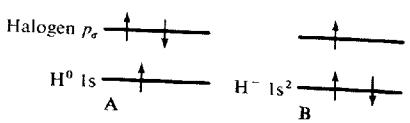
(*) After M. Wagner and J. M. Spaeth, 1973, to be published.

halides, but interestingly enough it is larger than the first shell value in KBr, showing that a special mechanism must exist which reduces so much the unpaired spin density at the nearest alkali neighbours.

I can only briefly mention that also centres with the hydrogen on substitutional halide sites were observed in alkaline earth fluorides [11], [12] and some alkali halides by the Oxford group [13]. The substitutional centres in CaF_2 were studied intensively by ENDOR [11].

From a theoretical point of view it would also be desirable to study hydrogen centres in LiF. ESR spectra of tritium centres after neutron irradiation of LiF could be observed by Causa, Raoux and Taupin [14] and Kazumata [15], however the precise atomistic structure of the centres has not yet been established unambigously.

2.2 THEORETICAL INTERPRETATION. — Attempts to calculate the ground state wave function for the interstitial centres in alkali halides have been made by several authors [16]-[23]. Very early Mimura and Uemura [16] have adopted Gourary and Adrian's method [24] of orthogonalising an envelope function to the cores of the nearest neighbour ions taking as wave functions for the lattice ions the free ion Hartree Fock wave functions as was done so far in all theoretical work. Their calculation could not explain the large anisotropy of the centre electron distribution and not the transfer effect to the outer shells. It was then realised by Spaeth [7] that it is decisive to take the overlap between neighbouring lattice ions into account or, in other words, to ensure that the free ion wave functions of the neighbour ion cores be mutually orthogonal. It could be shown that orthogonalisation of the unchanged hydrogen 1s function to such an orthogonalized set of free ion functions can qualitatively explain the spin density transfer to the outer shells and the small value of the spin density at the nearest alkali neighbours. Sammel [17] attempted to take into account in addition to the complete orthogonalisation the electrical crystal field and exchange interactions between the hydrogen atom and the nearest neighbours in an *ab initio* variational calculation minimizing the energy for KCl and NaCl. This led to some admixture of hydrogen 4f and 5g functions to the 1s function. He could not explain the low spin density at the nearest alkali neighbours, the result was in fact worse than in the above mentionned simple orthogonalisation. Cho, Kamimura and Uemura [18] tried another approach by considering a mixing of two possible configurations A and B for the ground state :



Configuration A consists of the hydrogen atom in the unperturbed lattice symbolized by the full valence band which is composed of the outer halogen p orbitals. Configuration B, which is slightly admixed into A, consists of a hole in the nearest halogens and a negatively charged hydrogen ion. The consideration of a hole state was suggested by the positive g-shift which is observed in most alkali halides.

Cho [19] treated the problem for KCl as a three particle problem taking into account the fact that in the H^- the two 1s orbitals with spin up and down are different from each other and different from the 1s orbital in H^0. Unfortunately Cho fitted the two necessary admixing parameters for the configurational mixing to the most critical experimental values, namely the isotropic shf constant for the nearest K nuclei and the proton hf constant, which should be explained by a theory, rather than being used for fitting. It should also be mentionned that in all theories so far the explanation of the observed proton hf constant caused special difficulties. Cho obtained rather poor agreement for the shf interactions of the higher Cl shells, the reason probably being that he overlooked the effect of the zero point vibrations.

We still think that basically the configurational mixing is so far the best description of the ground state although one would wish to determine the mixing parameters from first principles rather than by fitting to experimental results. In view of the many experimental data in various alkali halides [10] obtained since Cho's calculations Spaeth and Seidel [23] tried to estimate the shf interactions with a simplified version of Cho's picture by using a one particle approach in neglecting the differences between the various hydrogen 1s orbitals. The configuration mixing is then equivalent to a covalent admixture of some outer halogen p_σ-orbitals into the hydrogen 1s function. By fitting the covalency parameter to the experimentally observed first shell anisotropic halogen shf constants the spin density transfer to all higher shell nuclei can be well explained and also the low spin density at the nearest alkali neighbours is explained including the strange rise of $a(K^1)$ in KI (see Table I). The explanation is based on the combination of covalency and ion overlaps. In fact, the unpaired spin density at the nearest alkali nuclei comes out too small in this static calculation. This is rather nice since ENDOR results of deuterium centres have shown that a large fraction of the observed isotropic shf constant at the first shell alkali nuclei is only due to the zero point vibrations of the hydrogen atom with a rather large amplitude, that is purely dynamical in nature [25].

There is also other direct experimental evidence for a localised vibration of the interstitial hydrogen atom. In CaF_2 Shamu, Hartmann and Yasaitis [26] observed an infrared absorption at 15.5 μ. From their results they determined an effective Szigeti charge of 0.07. This charge is due to the overlaps of the hydrogen atom with the neighbours and is of the order one

would expect on the basis of the ENDOR results for the ground state. The existence of localised vibrational modes shows also up in the pressure effects on the F shf interaction studied by Blum [27] and the spin lattice relaxation investigated by Feldmann, Castle and Murphy [28].

Before turning to the optical experiments and the excited states I should like to remark that in view of the many precise experimental results about the ground state — only the most prominent results could be mentionned in this short review — a rigorous theory is called for. In the alkaline earth fluorides very little theoretical work was done so far. I feel that complete orthogonalization will always remain a central point of such a theory. Hopefully covalency appears from first principles and not as an adjustable parameter and also other effects such as crystal field, exchange, van der Waals interactions and zero point vibrations are considered together at all stages of the calculation.

3. **Optical investigations and the excited states.** — The interstitial centres in the alkali halides have optical absorption bands in the UV region. In figure 6 the peak positions of the main absorption bands are plotted versus the distance between the hydrogen atom and the nearest neighbours. The data are taken from the work of Fischer [29]. The absorption occurs between about 5.5 eV and 3.5 eV. This transition energy is much lower than the value of about 10 eV which one would expect for a hydrogen 1s-2p transition. Already in the early work of Kerkhoff, Martienssen and Sander [3] it was suggested that the optical transition is in its nature a charge transfer type transition where roughly speaking a halogen p electron goes over to the hydrogen atom forming H^- and leaving a hole in the halogens. (We have already considered a slight admixture of such a configuration to the unperturbed hydrogen in order to explain the structure of the ground state.) A rough estimate of the transition energy considering electron affinities and Madelung energy gives values about 0.5 to 1 eV higher than the observed ones and explains qualitatively the decrease in energy with increasing lattice constant [3], [29]. Fischer [29] looked more carefully at the absorption and found that it consists of several absorption bands. In figure 7*a* the 3 absorption bands in KI are shown. The doublet band U_2^1 and the band U_2^2 are due to the interstitial hydrogen centres, the band at the lowest energy is due to S^- centres which were produced simultaneously. The splitting between the U_2^1 and U_2^2 bands is nearly 1 eV in the iodides, it is 0.5 eV in the bromides and not resolved in the chlorides. The nature of the 3 transitions was cleared up by magneto-optical experiments done by Cavenett *et al.* [30] from the Oxford group and by Jacobs and Ingels [31]. Figure 7*b* shows the magnetic circular dichroism [30] which has a large paramagnetic part indicating a large spin orbit coupling in the excited state. Since spin orbit coupling is negligible from the hydrogen atom alone this result proves clearly that the excited state is of the charge transfer type. The magnetic circular dichroism changes sign within the U_2^1 doublet band and within the U_2^2 band showing that the spin orbit

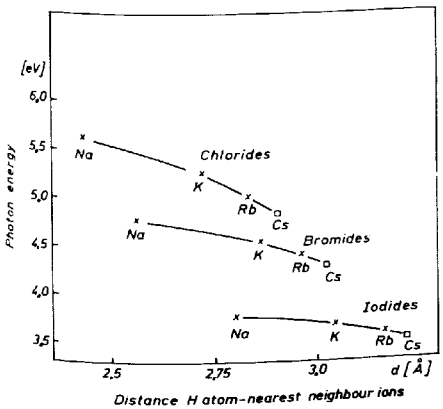


FIG. 6. — Transition energies of the main optical absorption bands U_2^1 of the interstitial hydrogen centres in the alkali halides. After Fischer [29].

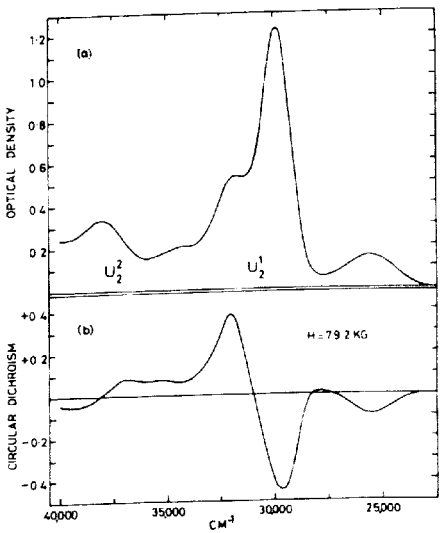


FIG. 7*a*. — Optical absorption bands U_2^1 and U_2^2 of interstitial hydrogen centres in KI. (Difference in the optical density of a crystal of KI : SH before and after ultraviolet irradiation at 4 K.)

FIG. 7*b*. — Magnetic circular dichroism. $H = 79{,}2$ kG. After Cavenett *et al.* [30].

structure exists within the U_2^2 band and within the U_2^1 band and not between the two bands wich was assumed at first when one interpreted the splitting between the U_2^1 and U_2^2 bands to be due to the atomic I spin orbit splitting [29]. It was shown by Gee, Hayes and O'Brien [32] that the two transitions U_2^1 and U_2^2 are from the A_1 ground state to the symmetry allowed $T_{2\sigma}$ and $T_{2\pi}$ linear combinations of the outer halogen p orbitals whereby these two excited states are mixed to some degree due to interactions between the 4 halogens. The observed circular dichroism arises because of this mixing.

To the authors knowledge so far no optical absorption has been observed for the hydrogen centres in the alkaline earth fluorides and the alkali fluorides. Neither a fluorescence emission could be observed, also not in the other alkali halides.

4. **Recent results in mixed alkali halides.** — In the last section of this review I would like to mention briefly some results we obtained in our Stuttgart group recently for interstitial centres in mixed alkali halides. If one replaces one of the 4 halogen neighbours by a heavier halogen ion, say one of the 4 Cl^- in KCl by Br^- or I^-, then this configuration proves to be a lower trap for the hydrogen atoms than the regular configuration with the 4 Cl^- ions. In KCl doped with a few percent Br^- or I^- one can produce interstitial hydrogen centres in the usual way by decomposing OH^- or SH^- centres and gets hydrogen centres in the mixed configuration according to the statistical chances. If one anneals the crystals then about 10 K below the decay temperature of the centres, the hydrogen atoms diffuse through the lattice and get trapped preferentially at those mixed configurations. In KCl or RbCl doped with I^- over 90 % of the hydrogen centres can be converted into the mixed configuration. Figure 8 shows the absorption spectrum

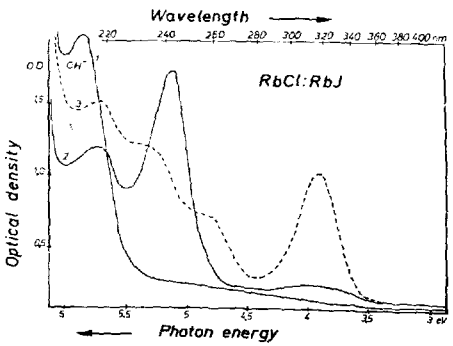


FIG. 8. — Optical absorption of interstitial hydrogen centres in RbCl doped with 0.8 % RbI. Curve 1 : crystal as grown containing I^- and OH^- at 77 K. Curve 2 : after 90 min. UV irradiation at 8 K. Curve 3 : after 120 min. annealing at 120 K, measured at 8 K. After Reuter [33].

for RbCl doped with I^- (G. Reuter and J. M. Spaeth, to be published). Curve 2 is obtained after decomposition of OH^- centres at low temperature and consists besides of some residual OH^- centres of the hydrogen absorption band peaking at 5.1 eV and a small band peaking at 3.9 eV due to some mixed centres according to the statistical chances. After annealing one obtains curve 3. The 3 absorption bands peaking at 5.3 eV, 4.80 eV and 3.90 eV are due to hydrogen atoms in the mixed configuration. From bleaching experiments with polarised light we concluded that the two low energy bands with a height ratio of about 2 : 1 are due to I^- transitions and the band peaking at 5.3 eV is due to Cl^- transitions. The latter is shifted somewhat to higher energy compared to the normal configuration. The large splitting of about 1 eV between the I^- bands may be due to the I spin orbit interaction. Magneto-optical experiments are under way to check this. ESR experiments proved that indeed the mixed configuration described above is realised. Figure 9 shows the ESR spectrum for KCl doped with Br^-

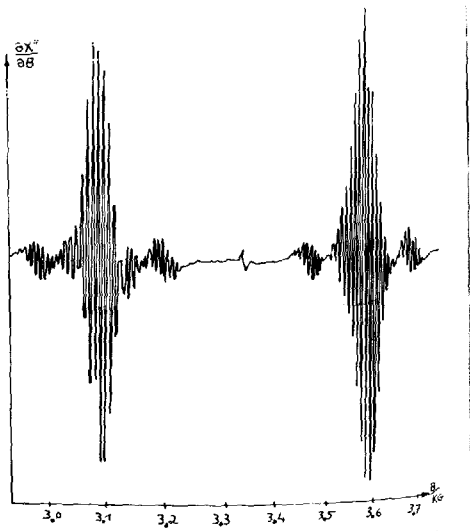


FIG. 9. — ESR spectrum of interstitial hydrogen centres in KCl doped with 2,5 % KBr. $B_0 // [100]$, ν_{ESR} = 9,38 GHz, T = 82 K. After Schwan [34].

(L. Schwan and J. M. Spaeth, to be published). The two line groups with large intensity are from the centres in the normal configuration (see Fig. 3). The additional 4 line groups at each proton line are due to the mixed configuration, the splitting into the 4 line groups is due to the Br shf interaction. Each of the Br shf line groups consists of 10 lines due to the shf interaction with the remaining 3 Cl neighbour nuclei. The Br shf interaction is about 50 % higher than the

one found in KBr for the normal configuration. A theoretical analysis shows that the Br covalency increases much more than one would expect from the increased overlap considering that the Br^- is squeezed into the smaller KCl lattice and assuming that covalency is proportional to overlap as is often done.

Finally I would like to mention that we observed a fluorescence emission from the mixed hydrogen centres in the chlorides doped with I^-. (F. Lohse, H. J. Paus, and J. M. Spaeth, to be published.) In RbCl : RbI one observes two emission bands, one in the blue region at 2.90 eV and one at 1.86 eV. Figure 10 shows the excitation spectrum. The emission at 1.86 eV can be excited in all three absorption bands whereas the emission at 2.90 eV can only be excited in the one I^- absorption band at higher energy and in the Cl absorption band. The two emission bands have their transition moment always parallel to the [111] direction which connects the hydrogen atom with the one I^- neighbour no matter where the excitation occurred. If one excites in the Cl absorption band, the exciting electrical vector has to be perpendicular to that [111] direction, whereas in the two I^- bands it is parallel. This result suggests that after excitation to the Cl charge transfer states a relaxation occurs into essentially I^- charge transfer states from which alone the fluorescence emission occurs.

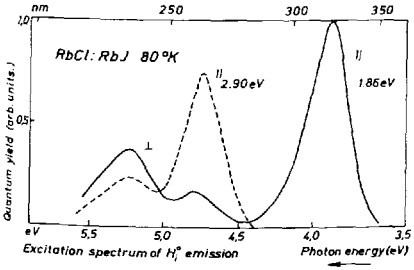


FIG. 10. — Excitation spectrum for the fluorescence emission bands at 2.90 eV and 1.86 eV of interstitial hydrogen centres in RbCl doped with 0.8 % RbI. $T = 80$ K. After Lohse [35].

5. **Conclusion.** — Let me remark as a conclusion to this review of the work done on atomic hydrogen centres, which of course had to be rather sketchy and uncomplete, that I feel that this type of defect can be looked upon as the « *hydrogen problem of the point defect* » and that one should be able to understand all properties of the centres quantitatively on the basis of calculations from first principles. The understanding of the ground state is already somewhat advanced, however the excited satte is still very much an open problem. Certainly also a lot of valuable information can be obtained about the electronic structure of the host lattices by further studies.

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