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Atomic Hydrogen at Anion Sites in LiF–H$^-$ and Na–H$^-$ Crystals

By

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Anion hydrogen atom centres are studied by optical and ESR techniques in LiF–H$^-$ and NaF–H$^-$ crystals. The ESR spectra of these centres are observed after X-ray irradiation of the crystals at 77 K. The optical absorption spectra of $H^0_{s,a}$ centres consist of two bands at 2.4 and 3.5 eV for LiF–H$^-$ and at 2.95 and 3.8 eV for NaF–H$^-$, which are due to the electron charge transfer from a fluorine ion to the 1 s state of the hydrogen atom.

Оптическими и ЭПР методами исследованы атомарные центры водорода в кристаллах LiF–H$^-$ и NaF–H$^-$. ЭПР спектры этих центров наблюдаются после рентгеновского окрашивания кристаллов при 77 K. Спектры оптического поглощения $H^0_{s,a}$-центров состоят из двух полос при 2,4 и 3,5 eV в LiF–H$^-$, и 2.95 и 3,8 eV в NaF–H$^-$. Эти полосы поглощения обусловлены переносом электрона с иона фтора на 1 s уровень водорода.

1. Introduction

Atomic hydrogen can be trapped at interstitial or substitutional cation and anion sites in alkali halides. The anion centres ($H^0_{s,a}$ or U_3) are produced by X-ray irradiation at 77 K of crystals containing U centres ($H^-_{s,a}$ centres). The number of centres could be enhanced by an order of magnitude by doping the crystals with Ag^+ ions, which act as electron traps. The ESR spectrum of these centres shows two proton hyperfine (HF) lines separated by approximately the HF constant of the free hydrogen atom, but the additional superhyperfine (SHF) structure is usually unresolved because of the weak SHF interaction with neighbouring nuclei. The comparatively weak SHF interaction in these centres could be resolved by ENDOR experiments.

U_3 centres have been studied by ESR in NaCl [1], KCl, RbCl, KBr [2] crystals, but only in two of them, KCl [3] and RbCl [4], ENDOR investigations were performed.

There are some works dealing with the atomic hydrogen centres in LiF crystals produced by γ- or neutron-irradiation [5 to 7]. After vacuum-UV irradiation of OH$^-$ doped LiF the ESR spectrum of atomic hydrogen with HF splitting of 502×10^{-4} T and peak to peak linewidth of 10×10^{-4} T has been observed by Hoentzsch and Spaeth [8]. According to these authors the atomic hydrogen, probably, occupies an anion site.

Hydrogen or tritium atoms produced by γ- or neutron-irradiation show much smaller linewidth than should be expected [5 to 7], indicating that they occupy no lattice or interstitial sites but cavities created by irradiation damage or plastic deformation.

In our previous work [9] we found that X-ray irradiation of LiF–H$^-$ crystals at 77 K leads to the creation of atomic hydrogen centres, which were assigned to the interstitial

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hydrogen atom based on the H_2^--centre formation ($H_i^0 + H_{s,a}^- \rightarrow H_2^-$). New data of ESR and optical measurements in LiF–H$^-$ and NaF–H$^-$ reported in this paper are not consistent with this model.

2. Experimental Technique

The experimental technique and the preparation of the crystals have been described elsewhere [9]. The LiF–H$^-$ crystals used in this work contained 10^{17} to 10^{20} cm^{-3} U centres, and the concentration of U centres in NaF–H$^-$ crystals range from 10^{17} to 10^{18} cm^{-3}. The concentration of H$^-$ ions was determined by infrared spectroscopy using the characteristic absorption of these ions. No trace of OH$^-$ ions could be found by infrared spectroscopy in LiF–H$^-$ crystals, but NaF–H$^-$ crystals contain a small amount of OH$^-$ centres. The crystals were irradiated by X-rays from a Pd tube operating at 40 kV and 50 mA.

3. Results

3.1 ESR

In our previous paper [9] we found that X-irradiation of LiF–H$^-$ crystals at 80 K leads to the creation of atomic hydrogen centres, which have a doublet ESR spectrum with splitting between lines of 518×10^{-4} T. The observed two proton HF lines were inhomogeneously broadened by unresolved SHF interactions and the linewidth ΔB (peak to peak) was 45×10^{-4} T. However, recently we found, using crystals with higher hydrogen concentration (10^{20} cm^{-3}) that these centres saturate readily at 80 K and the decrease of microwave power leads to the appearance of the SHF structure. For $\boldsymbol{B} \parallel \langle 111 \rangle$ each broad line is split into seven lines equally spaced by 18×10^{-4} T in normal LiF–H$^-$ as well as in crystals enriched to 90% with ^{6}Li (Fig. 1a). For $\boldsymbol{B} \parallel \langle 110 \rangle$, the partly resolved SHF structure is only observed in LiF–H$^-$ enriched in ^{6}Li. Measurements of the average splitting between the lines gave the result 4.5×10^{-4} T (Fig. 1b).

A similar ESR spectrum was first observed in γ-irradiated LiF–OH$^-$ by Akhvlediani et al. [10] who assigned the ESR signal to the unperturbed hydrogen atom in a cation vacancy ($H_{s,c}^0$ centre). However, the SHF structure is only resolved for $\boldsymbol{B} \parallel \langle 111 \rangle$ and this is not sufficient for a correct conclusion, and the observed SHF structure for $\boldsymbol{B} \parallel \langle 110 \rangle$ in the case of ^{6}LiF–H$^-$ could not be consistent with this model. Furthermore, $H_{s,c}^0$ centres are usually formed in crystals additionally doped with divalent cations, but in the latter case the crystals used are not doped with divalent metals and the source of the cation vacancies is not clear. Moreover, in LiF–H$^-$, Mg^{2+} crystals, the ESR spectrum of atomic hydrogen with a well-resolved SHF structure in all directions was observed. The analysis of the spectrum allows us without doubt to assign it to an unperturbed hydrogen atom at a cation vacancy [11].

In spite of the similarity of both ESR spectra, the results strongly differ in the temperature dependence of the destruction of the centres. Whereas in γ-irradiated LiF–OH$^-$ the atomic hydrogen centres are thermally stable up to 520 K [10], in LiF–H$^-$ they began to be destroyed at 110 K. There are a few steps of thermal destruction of these centres. The thermal destruction is entirely finished at about room temperature [12]. Perhaps, in γ-irradiated LiF–OH$^-$ crystals the atomic hydrogen is stabilized by neigbouring defect.

Since the anion atomic hydrogen centres are usually produced by X-irradiation of alkali halides containing U centres, we assume that the spectrum is due to atomic hydrogen at an anion site.

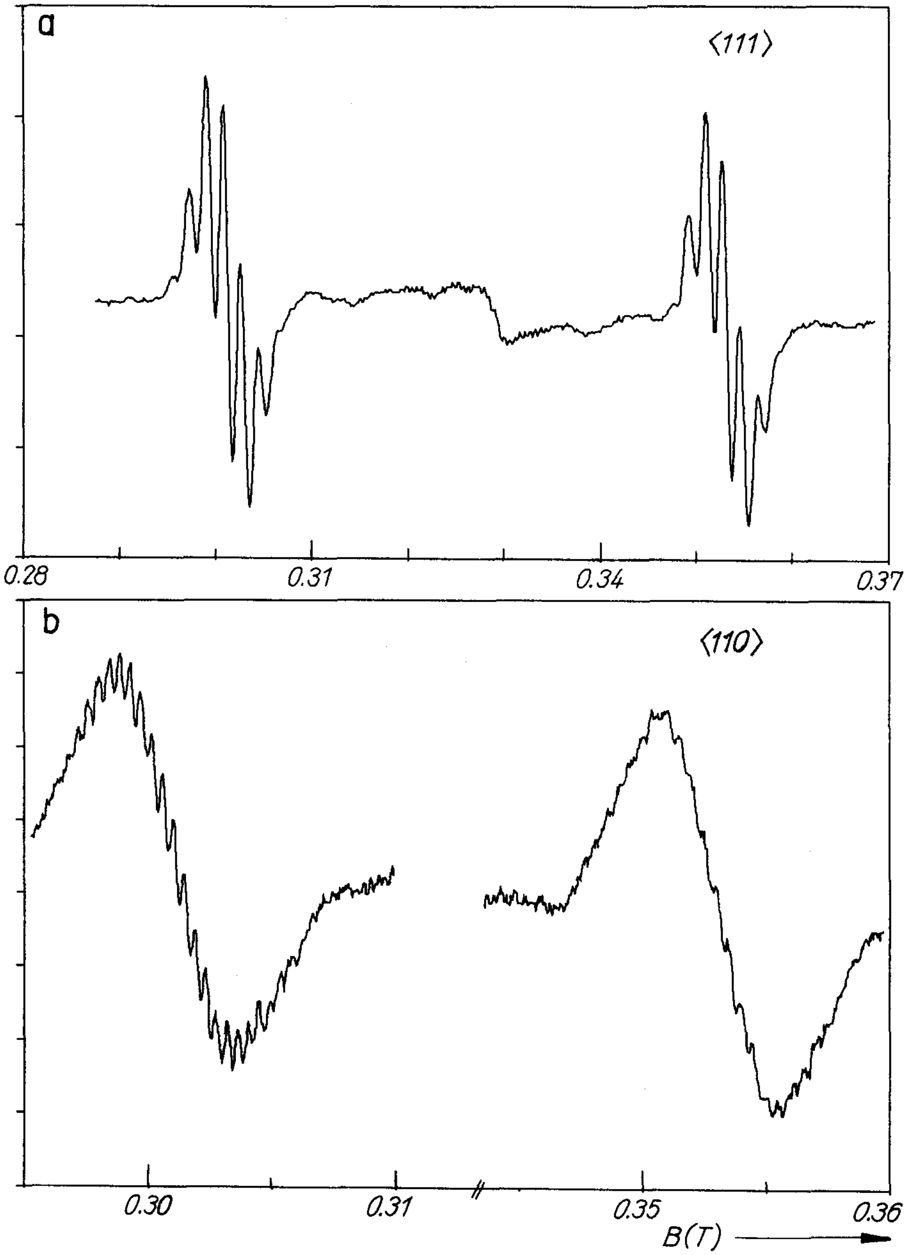

Fig. 1. ESR spectrum of $H^0_{s,a}$ centres in LiF–H^- after X-irradiation at 77 K for a) $\boldsymbol{B} \parallel \langle 111 \rangle$ ($\nu = 9234.0$ MHz) and b) $\boldsymbol{B} \parallel \langle 110 \rangle$ ($\nu = 9237.0$ MHz)

In order to explain the SHF structure of the ESR spectrum we must make the following assumptions. First, the SHF structure is due to the interaction with the neighbouring nuclei of the second shell, but not with those of the first, i.e. $a_F \gg a_{Li}$. Second, the anisotropic part of the SHF interaction is close to the isotropic part, i.e. $a_F \approx b_F$.

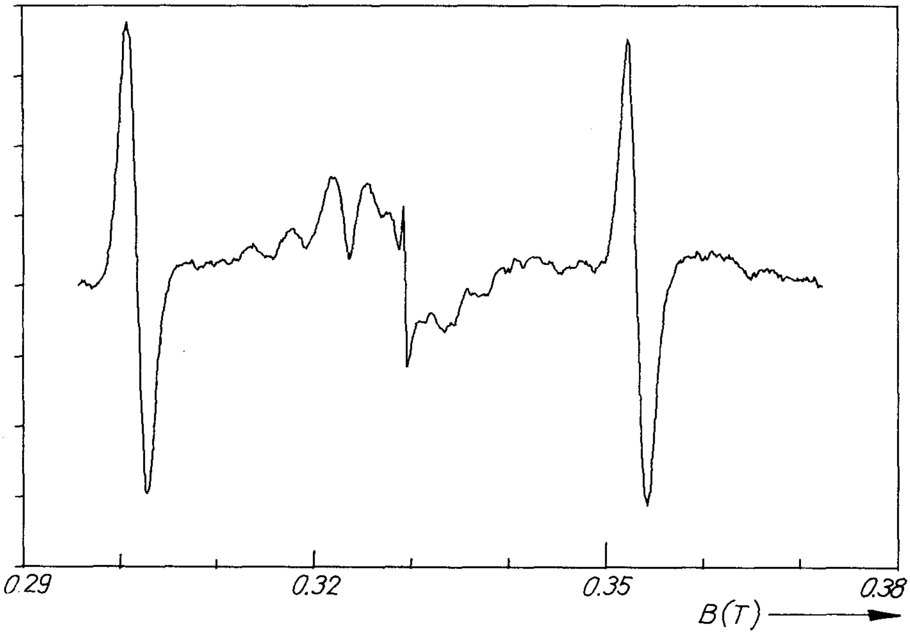

Fig. 2. ESR spectrum of $H^0_{s,a}$ centres in NaF–H^- after X-irradiation at 77 K, ν = 9238.7 MHz

Under these assumptions, for $\boldsymbol{B} \parallel \langle 111 \rangle$, one would expect seven SHF lines and seven are observed with the splitting between lines being equal to $[(a_F + b_F)^2 + 2b_F^2]^{1/2}$. From this follows $a_F = 7.3 \times 10^{-4}$ T. For $\boldsymbol{B}$ aligned parallel to $\langle 110 \rangle$, the spectrum is expected to consist of thirteen transitions with a splitting of $1.5a_F$. The inspection of the spectrum shows more than thirteen lines (Fig. 1b) with a splitting of 4.5×10^{-4} T, this is of about two times less than one would expect. It is not improbable that the additional lines observed between the main lines arise from "forbidden" transitions because the structure of the low-field component differs from that of the high-field component.

The first assumption is also supported by consideration of F centres because it also has a 1 s electron on an anion vacancy. In this case the isotropy constant of the second shell is by a factor 2.5 larger than that of the first shell. The difference should be increased in the case of an anion hydrogen atom because of the relaxation of the lattice around the atomic hydrogen. Due to the effective positive charge of the vacancy the surounding Li^+ ions are repelled and the F^- ions of the second shell are attracted.

For anion hydrogen centres a strong anisotropic interaction is observed and in KCl the isotropic and the anisotropic constants are of the same order [3].

Table 1

Proton HF constants a_p, A_p, g-factor, and linewidth (peak to peak) ΔB of anion hydrogen atom centres in LiF and NaF

crystal	g	A_p (MHz)	a_p (10^{-4} T)	ΔB (10^{-4} T)
LiF	2.0022 ± 0.0004	1440 ± 4	518 ± 2	45
NaF	2.0022 ± 0.0003	1439 ± 3	517 ± 2	22

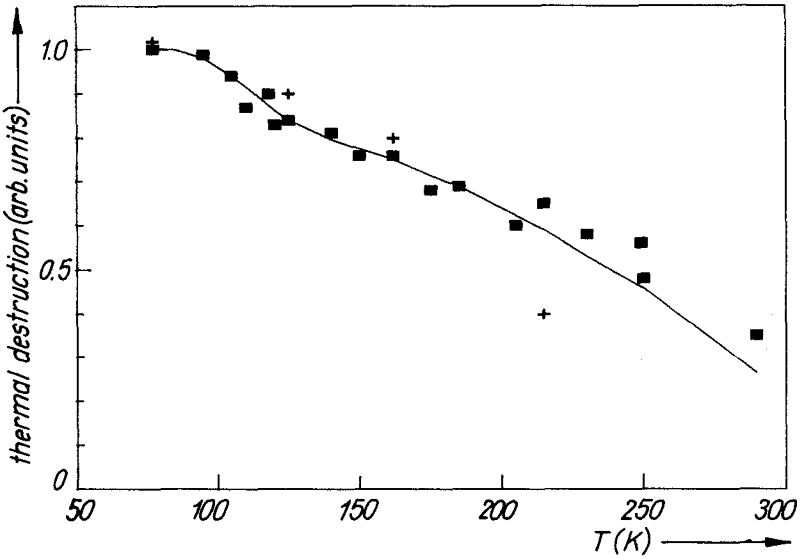

Fig. 3. Thermal stability of $H^0_{s,a}$ centres in NaF–H$^-$ as determined from the disappearance of ESR signal (■) and optical absorption (+)

X-irradiation of NaF–H$^-$ crystals at 77 K leads to the formation of atomic hydrogen centres, which have an ESR spectrum as shown in Fig. 2. The observed two proton lines separated by 517×10^{-4} T are inhomogeneously broadened by unresolved SHF interactions. The linewidth (peak to peak) is 22×10^{-4} T. Values of the ESR parameters for this centre are given in Table 1.

The temperature dependence of the destruction of these centres is shown in Fig. 3. As in the LiF–H$^-$ case [12], there are a few steps of thermal destruction of the hydrogen atom centres in the temperature range from LNT to RT. The temperature of the last step of the thermal destruction of these centres in NaF–H$^-$, as well as in the case of LiF–H$^-$, is close to the temperature of migration of anion vacancies in these crystals.

Comparing the results on both crystals, we may conclude that in NaF–H$^-$ the hydrogen atom produced by low-temperature X-irradiation is located in an anion vacancy as in the case of LiF–H$^-$. In both crystals the thermal or optical bleaching of the anion hydrogen atoms leads to the formation of H_2^- centres [13, 14]. Perhaps, the interstitial hydrogen atoms are formed after the destruction of anion hydrogen centres which are trapped at U centres ($H_i^0 + H_{s,a}^- \rightarrow H_2^-$).

3.2 Optical absorption

From the ESR data we made the assumption that the observed spectra in LiF and NaF airse from the hydrogen atoms at anion sites. The absorption of these centres is due to the electron charge transfer from a fluorine ion to the 1 s state of the hydrogen atom as it was assumed by Hayes and Hodby [1] in perfect analogy to the mechanism of the U_2 optical absorption [15]. The U_3 optical absorption energy is expected to be approximately equal to the difference between the electron affinity of hydrogen (0.75 eV) and of halogen [1]. The latter has a small change from F to I (F (3.4 eV)), Cl (3.62 eV), Br (3.36 eV), and I (3.06 eV).

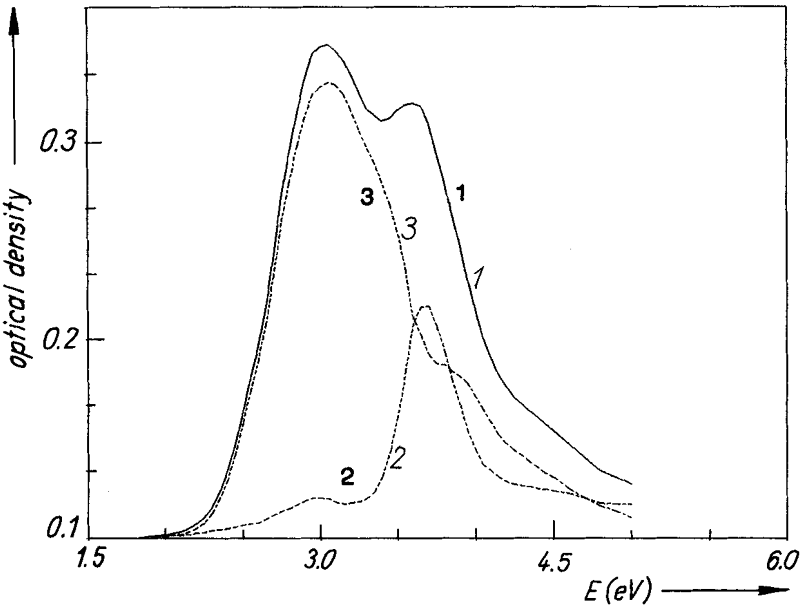

Fig. 4. Absorption spectra of NaF–H$^-$, (1) after X-irradiation at 77 K and (2) subsequent optical bleaching with light at 2.5 eV at 77 K. Curve (3) was obtained by subtracting curve 2 from curve 1

Therefore, the U_3 transition energy is expected to be in the range 2.8 to 3.5 eV in all alkali halides.

Optical bleaching experiments indicate that the U_3 centre in KCl has a weak absorption band peaking at 2.9 eV with a halfwidth of 1 eV [1] in good agreement with above-mentioned assumptions.

The formation of U_3 centres in LiF by low-temperature X-irradiation gives rise to two absorption bands at 3.5 and 2.4 eV [9, 12]. The energy difference between the bands is due to the σ–π splitting of t_{1u} states of fluorines. Assuming that the σ-transition is higher in intensity, we could interpret the bands at 3.5 and 2.4 eV as the $t_{1u}(\sigma) \rightarrow a_{1g}$ and $t_{1u}(\pi) \rightarrow a_{1g}$ transitions, respectively.

After X-irradiation of NaF–H$^-$ at 77 K the optical absorption spectrum below 6.2 eV consists of two bands, a strong band at 2.95 eV and a weaker one at about 3.8 eV (Fig. 4). These absorption bands are correlated with the electron spin resonance of the $H^0_{s,a}$ centres. On annealing at temperatures above 100 K the absorption bands and the $H^0_{s,a}$ centre ESR decrease simultaneously. On increasing the temperature to 300 K the absorption bands at 3.8 and 2.95 eV entirely disappear. Optical bleaching with visible light at 77 K leads to the disappearance of the $H^0_{s,a}$ centre ESR and the optical absorption bands at 2.95 and 3.8 eV and one can observe only a weak F absorption band at 3.7 eV which is hidden under the spectrum of $H^0_{s,a}$ centres at 77 K (Fig. 4, curve 2). From these results we can conclude that the bands at 2.95 and 3.8 eV are associated with the $t_{1u}(\sigma) \rightarrow a_{1g}$ and $t_{1u}(\pi) \rightarrow a_{1g}$ transitions, respectively, giving $\Delta(\sigma-\pi) = 0.85$ eV.

In the NaF–H$^-$ case, the $t_{1u}(\pi)$ level is below the $t_{1u}(\sigma)$ one because the band at 3.8 eV is smaller in intensity. The reverse situation is observed in the case of LiF–H$^-$, where the $t_{1u}(\pi)$ is the upper level.

In many alkali halides doped with impurity metals in which charge transfer transitions from a halide ion to the impurity metal are observed, the t(π) level is located above the t(σ) one [16]. On the other hand for all known H_i^0 centres in alkali halides t(σ) is the upper level [17]. It is possible that this is due to size effects of substitutional or interstitial sites.

References

[1] W. Hayes and J. W. Hodby, Proc. Roy. Soc. **A294**, 359 (1966).
[2] A. G. Badalayan and P. G. Baranov, phys. stat. sol. (b) **97**, 95 (1980).
[3] G. Heder, J. R. Niklas, and J. M. Spaeth, phys. stat. sol. (b) **100**, 567 (1980).
[4] G. Heder, J. R. Niklas, and J. M. Spaeth, Radiat. Eff. **73**, 61 (1983).
[5] M. T. Causa, D. Raoux, and Ch. Taupin, J. Phys. Chem. Solids **31**, 1011 (1970).
[6] E. Duval, J. Serughetti, and R. Lonaf, Solid State Commun. **8**, 1155 (1970).
[7] Y. Kazumata, phys. stat. sol. **25**, 563 (1968).
[8] Chr. Hoentzsch and J. M. Spaeth, Solid State Commun. **29**, 577 (1979).
[9] A. V. Egranov, V. V. Otroshok, and B. P. Chernyago, phys. stat. sol. (b) **167**, 451 (1991).
[10] Z. G. Akhvlediani, I. G. Akhvlediani, and T. L. Kalabegishvili, phys. stat. sol. (b) **119**, 503 (1983).
[11] A. V. Egranov, phys. stat. sol. (b) **179** 323 (1993).
[12] A. V. Egranov, A. I. Nepomnyachikh, V. V. Otroshok, and B. P. Chernyago, Optika i Spektroskopiya **66**, 1319 (1989).
[13] A. V. Egranov, A. I. Nepomnyachikh, V. V. Otroshok, and B. P. Chernyago, phys. stat. sol. (b) **155**, 365 (1989).
[14] A. V. Egranov, J. Phys.: Condensed Matter **4**, 9255 (1992).
[15] F. Kerkhoff, W. Martienssen, and W. Sander, Z. Phys. **176**, 305 (1963).
[16] M. Moreno, Solid State Commun. **29**, 653 (1979).
[17] B. C. Cavenett, J. V. Gee, W. Hayes, and M. C. M. O'Brien, Solid State Commun. **6**, 697 (1968).

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