*Vinogradov Institute of Geochemistry, Academy of Sciences of the USSR,
Siberian Branch, Irkutsk[1])*

H_2^--Centre in LiF–H$^-$

By

A. V. EGRANOV, A. I. NEPOMNYACHIKH,
V. V. OTROSHOK, and B. P. CHERNYAGO

The H_2^--centre in LiF is studied by optical and ESR techniques. The centre is produced by reaction between H_i^0 and H_a^--centres. The H_2^--centre ESR spectrum shows three broad lines which are due to the hyperfine interaction of an unpaired electron with the two protons. The resolved superhyperfine structure (as in case of F-centre) arises from the interaction with the lithium nuclei in a first shell and the fluoride nuclei in a second shell. Optical absorption band of the H_2^--centre at 5.05 eV is similar to that of the F-band, only slightly shifted to higher energies. The centre has the character of molecule-ion as well as of F-centre.

Оптическими и ЭПР методами исследованы H_2^--центры в кристаллах LiF–H$^-$. Эти центры образуются при взаимодействии H_i^0 и H_a^--центров. ЭПР спектр H_2^--центров состоит из трех широких линий, обусловленных сверхтонким взаимодействием с двумя протонами. Разрешенная суперсверхтонкая структура (как и в случае F-центров в LiF) обусловлена взаимодействием с ионами лития в первой сфере и ионами фтора во второй сфере. Полоса поглощения H_2^--центров при 5,05 eV близка к F-полосе поглощения. H_2^--центр проявляет свойства как молекулярного иона, так и F-центра.

1. Introduction

Hydrogen centres in various alkali halides have been intensively studied by optical and magnetic resonance techniques [1, 2]. Since atomic hydrogen is paramagnetic it could be studied with electron spin resonance (ESR) and electron nuclear double resonance (ENDOR). Various atomic hydrogen centres were investigated with these methods [3, 4]. Above LNT interstitial hydrogen atoms start to diffuse and can be trapped at the OH$^-$-centres to produce H_2O^--centres [5]. In SH$^-$-doped crystals KCl the H_2S^--centres are created [6]. These centres have been also studied by optical and magnetic resonance techniques.

It was shown in [7] that when LiF–H$^-$ crystals are X-irradiated at RT an electron spin resonance spectrum is observed. The ESR spectrum shows three broad lines with intensities in the ratios 1:2:1 which are due to the hyperfine (HF) interaction of an unpaired electron with the two protons. It was suggested [7] that the ESR spectrum is due to H_2^+-centres. However, the observed SHF structure could not be consistent with this model.

In our previous paper [8] we have shown that the centres related to the triplet ESR spectrum are produced (as in the cases of H_2O^- and H_2S^--centres) from interstitial hydrogen atoms. Through thermal annealing at about 110 K the interstitial hydrogen atoms diffuse and get trapped at H_a^--centres ((H_2^-)$_a$-centres).

This paper reports the results of electron spin resonance and optical absorption measurements of the (H_2^-)$_a$-centres in LiF–H$^-$ crystals.

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[1]) Favorskii street 1a, P.O. Box 701, SU-664033 Irkutsk, USSR.

2. Experimental Techniques

The LiF–H⁻ crystal were grown in a hydrogen atmosphere ($\approx 4 \times 10^5$ Pa) from the melt containing LiH by the Stockbarger method. Specimens of ^{6}LiF–H⁻ were obtained in a similar fashion. The starting material was polycrystalline ^{6}LiF enriched to 90% ^{6}Li. The crystal used in this work contained 10^{16} to 10^{20} cm⁻³ H_a^--centres [9]. Absorption measurements were performed with the spectrophotometer Specord UV/VIS.

The ESR experiments were done on an X-band spectrometer (RE-1306) in connection with a cryostat suitable for temperatures 80 and 295 K. The microwave frequency was measured by a frequency counter with accuracy of 1×10^{-6}. The magnetic field strength was controlled by a nuclear magnetic resonance gauss-meter outside the cavity and the DPPH sample inside.

The observation of the $(H_2^-)_a$-centre resonance is hindered by the presence of the paramagnetic F-centre. However, the F-centre resonance absorption is easily saturated in contrast to that of the $(H_2^-)_a$-centre. Since no saturation of the $(H_2^-)_a$-centre resonance absorption was observed, this ESR was detected at relatively high microwave power levels.

The crystals were X-rayed using a tungsten tube operating at 50 kV and 50 mA at 80 and 295 K.

3. Experimental Result

3.1 ESR spectra

In our previous paper [8] we found that X-irradiation of LiF–H⁻ crystals at 80 K leads to the creation of H_i^0-centres, which have a doublet ESR spectrum. Above 110 K the ESR spectrum of H_i^0-centres decreases and a new triplet ESR spectrum appears. This spectrum was also observed in LiF–H⁻ crystals X-irradiated at room temperature and is shown in Fig. 1. Parts a) and b) were obtained with the normal LiF–H⁻ crystal oriented so that B_0 was along $\langle 111 \rangle$ and $\langle 100 \rangle$ axes of the samples, respectively. The spectra contain the three broad lines with intensities in the ratios 1:2:1 and with HF constant $a = (26.06 \mp 0.03)$ mT. This fact indicates that the unpaired electron interacts with two equivalent hydrogen nuclei ($I = 1/2$). For $B_0 \| \langle 111 \rangle$ each broad line is split into many lines due to the SHF interaction with nearest neighbours. Measurements of the average splitting between the lines gave the result (0.75 ∓ 0.02) mT. The SHF structure strongly depends on the crystal orientation in the applied magnetic field B_0. A similar behaviour of a SHF structure was observed for F-centres in LiF crystals. The SHF structure of the F-centres in LiF arises from the interaction with the lithium nuclei in the first shell and with the fluorine nuclei in the second shell [10].

It may be proposed that in our case the SHF structure arises also from the interaction with ions of two shells. In order to check this assumption concerning the ESR spectrum in the normal LiF–H⁻ crystals, a study was made of the change in the spectrum to be expected if all the lithium atoms were the isotope ^{6}Li (normal lithium is 93% ^{7}Li, 7% ^{6}Li).

The ESR spectrum of X-irradiated ^{6}LiF–H⁻ at room temperature shows a well-resolved SHF structure quite different from that observed from normal LiF–H⁻. However, the SHF structure of each of the broad bands in ^{6}LiF–H⁻ is similar to that of the F-centre in ^{6}LiF crystals [10]. Electron spin resonance spectra of ^{6}LiF–H⁻ crystals X-irradiated at room temperature are shown in Fig. 2. Part a) was obtained for $B_0 \|$ $\| \langle 100 \rangle$ and part c) shows the low-field band of the triplet ESR spectrum for $B_0 \|$ $\| \langle 111 \rangle$. Measurements of the average splitting between lines (part c) gave the result
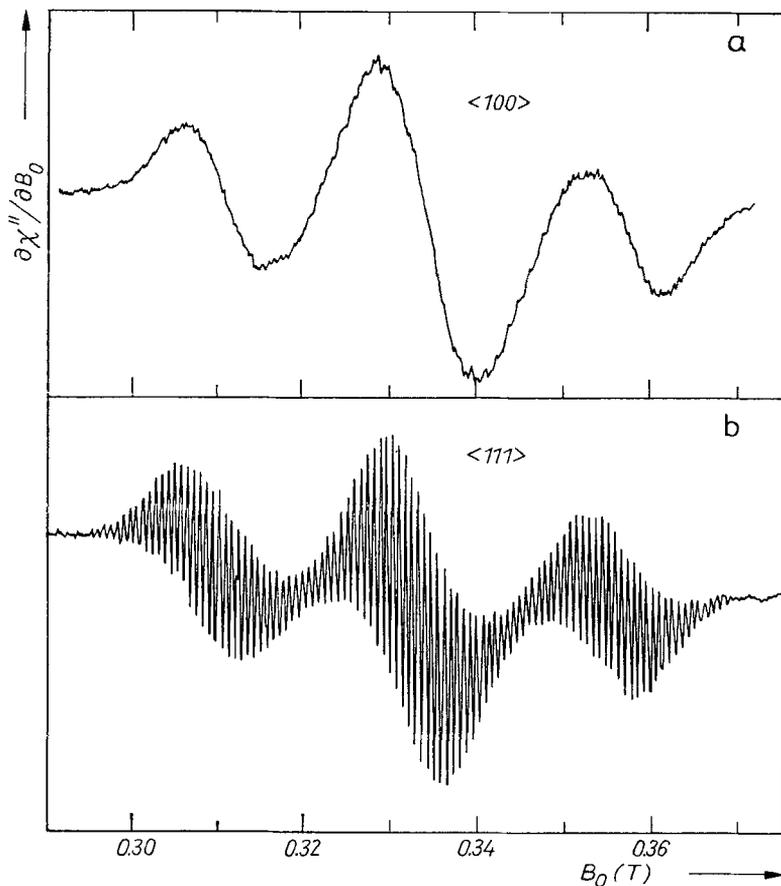
Fig. 1. ESR spectra of $(H_2^-)_a$-centres in normal LiF–H⁻. a) $\boldsymbol{B}_0 \parallel \langle 100 \rangle$, b) $\boldsymbol{B}_0 \parallel \langle 111 \rangle$; $T = 295$ K, $\nu_0 = 9343.8$ MHz

(0.31 ∓ 0.02) mT. For $\boldsymbol{B}_0 \parallel \langle 100 \rangle$ each broad band contains nine (as for F-centres) resolved lines equally spaced by (2.67 ∓ 0.03) mT (Fig. 2a).

From these results we came to the conclusion that the SHF structure in LiF–H⁻ crystals is similar to the SHF structure of the F-centres and arises from the interaction of the unpaired electron with lithium nuclei in the first shell and fluorine nuclei in the second shell. Therefore, the ESR spectrum is associated with the $(H_2^-)_a$-centres.

It should be noticed that the individual SHF lines are not expected to be resolved and many SHF lines segregate into a relatively small number of groups, which consist of the resolved SHF structure of the F- [10] and $(H_2^-)_a$-centres ESR spectra. However, it is to be expected that the $(H_2^-)_a$-centre spectrum in LiF (as in case of the F-centre) will show a splitting related directly to the shell-1 and shell-2 isotropic SHF coupling constants [10]. The SHF coupling constants for the F-centres and splitting between lines for the F- and $(H_2^-)_a$-centres are included in Table 1.

From Table 1, it is seen that the isotropic SHF constants of the F-centres are roughly correlated with the splittings between the lines. The F-centre spectrum in ⁶LiF is unusual in that it possesses a SHF structure in which contributions from the
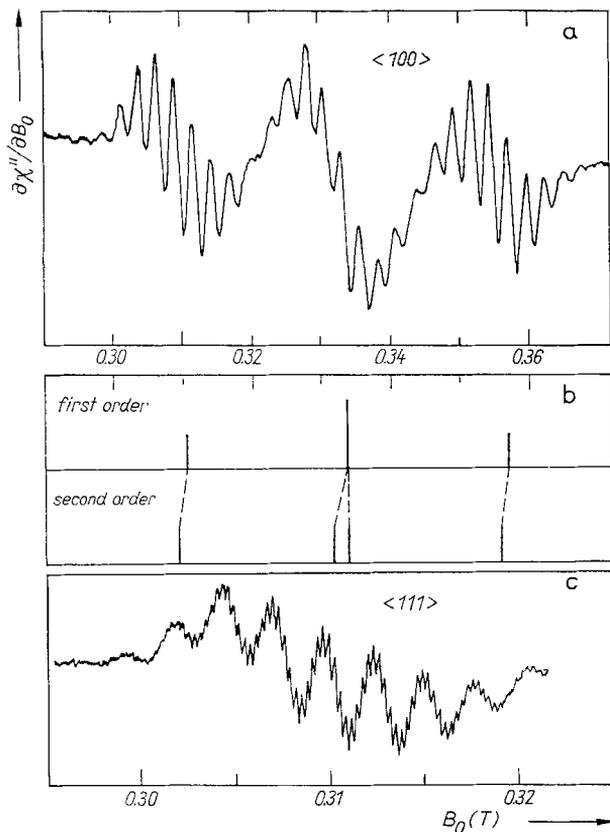
Fig. 2. ESR spectra of $(H_2^-)_a$-centres in ^{6}LiF–H$^-$. a) $\boldsymbol{B_0} \parallel \langle 100 \rangle$, c) low-field component of the triplet for $\boldsymbol{B_0} \parallel \langle 111 \rangle$; $T = 295$ K, $\nu_0 = 9343.8$ MHz. b) Position and intensities of first- and second-order HF splitting

first and second shells of neighbouring nuclei may be individually identified. Following Kaplan and Bray [10] we assume that the main splitting, which is observable in Fig. 2 (^{6}LiF, $\boldsymbol{B_0} \parallel \langle 100 \rangle$), arises from the isotropic interaction with the fluorine nuclei in the second shell ($a_{19\mathrm{F}} \approx 2.67$ mT). The resolved smaller splittings which are observed for $\boldsymbol{B_0} \parallel \langle 111 \rangle$ (Fig. 1 b and Fig. 2 c) result from the isotropic interaction with the lithium nuclei in the first shell ($a_{6\mathrm{Li}} \approx 0.31$ mT, $a_{7\mathrm{Li}} \approx 0.75$ mT).

Table 1

Isotropic SHF coupling constants of the F-centre a (mT) and splittings for the F- and $(H_2^-)_a$-centres in LiF

shell	nucleus	a (mT) [10]	splitting (mT) for F-centres [10]	splitting (mT) for $(H_2^-)_a$ centres
1	^{7}Li	1.394	1.47	0.75 $\mp$ 0.02
2	^{19}F	3.780	3.91	2.67 $\mp$ 0.03
1	^{6}Li	0.5279	0.56	0.31 $\mp$ 0.02

3.2 Absorption spectra

Since the unpaired electron is in a $(H_2^-)_a$-centre spread out over many shells of neighbouring ions in the way very similar to the F-centre, it is to be expected that the absorption spectrum of the $(H_2^-)_a$-centre will show the perturbed F-absorption band (as in case of the H_2O^--centre [5]).

As mentioned above in our previous paper [8] it was reported that the $(H_2^-)_a$-centre is created after thermal decay of H_i^0-centres. X-irradiation of LiF–H⁻ crystals at 80 K produced interstitial hydrogen atoms according to [11]

$$H_a^- \rightarrow F + H_i^0 . \tag{1}$$

Upon annealing the H_i^0 vanishes and the $(H_2^-)_a$-centre appears, which is interpreted as a result of the reaction

$$H_i^0 + H_a^- \rightarrow (H_2^-)_a . \tag{2}$$

When crystals of LiF–H⁻ are irradiated at 80 K, the optical absorption spectra above 200 nm consist of three bands, the F-band in ultraviolet at 5.0 eV and additional bands at 3.5 and 2.4 eV (Fig. 3). It has been shown that the latter absorption bands are associated with electron spin resonance of the H_i^0-centres [8]. Above 110 K these absorption bands and the H_i^0-centre ESR are decreased simultaneously and the $(H_2^-)_a$-centre ESR and a new absorption band at 5.05 eV appear. The optical absorption of this band is very similar to that of the F-centre, only shifted to slightly higher energies.

Optical bleaching with light of 3.72 eV at 80 K leads to the disappearance of the H_i^0-centre ESR and the optical absorption bands at 3.5 and 2.4 eV and to the creation of an absorption band at 5.05 eV (Fig. 3, curve 2). Apparently, the excitation light stimulates the migration of the H_i^0-centres at 80 K.

Above 390 K the $(H_2^-)_a$-centre is destroyed and the disappearance of the $(H_2^-)_a$-ESR is correlated with that of the absorption band at 5.05 eV (Fig. 4). Taking into account
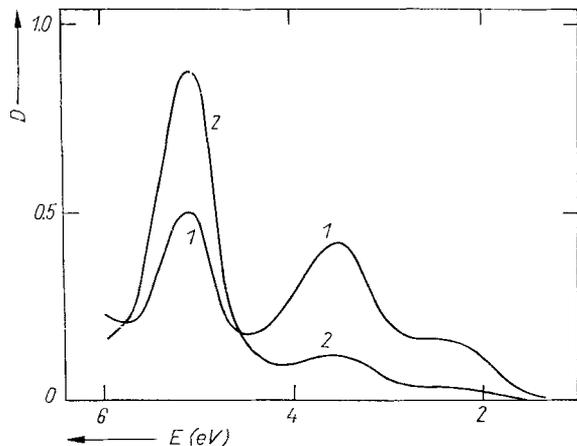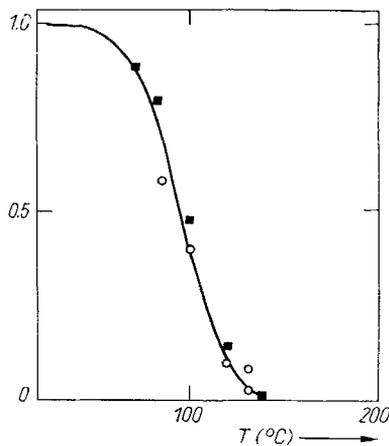

Fig. 3   Fig. 4

Fig. 3. Absorption spectra of LiF–H⁻ at 80 K. (1) After X-irradiation at 80 K and (2) optical bleaching with light of 3.72 eV at 80 K

Fig. 4. Thermal stability of $(H_2^-)_a$-centres $\partial\psi''/\partial B_0$ in LiF–H⁻ as determined by the disappearance of ESR signal (■) and optical absorption band at 5.05 eV (○)

these facts we came to the conclusion that the absorption band at 5.05 eV in LiF–H$^-$ is associated with the $(H_2^-)_a$-centre and absorption is due to (as in case of the H_2O^--centre [5]) electronic transitions of the perturbed F-centre (F-centre with an embedded hydrogen molecule — $F(H_2)$-centre, which is chemically equivalent to H_2^- on an anion site).

3.3 g-factor

The g-factor and the proton HF constant were determined from the centres of the SHF groups for $B_0 \parallel \langle 111 \rangle$. The g-values of ^{6}LiF and normal LiF of $(H_2^-)_a$-centre spectra are isotropic and within the uncertainty of the experiment equal to $2.0074 \mp \mp 0.0003$.

Since the proton HF energy and even the SHF energies of the nearest neighbours are not very small compared to the electron Zeeman energy, it is necessary to consider the higher-order corrections. A perturbation calculation to second-order HF splitting [12] leads to a removing of the energy level degeneracy and the central HF component is split into two bands. In this case it is expected that the ESR spectrum will show four HF components with equal intensities (Fig. 2 b). However, the two components of the central bond overlap strongly and the second-order HF splitting is well observed in ^{6}LiF crystals only. From Fig. 2 a, it is seen that there is a slight difference between the SHF structure of the central band and that of the outer bands. This could be due to a superposition of the second-order HF components of the central band. More difficultly this difference is observed in normal LiF crystals (Fig. 1).

The corrected g-value may be obtained from the equations [12]

$$H_k = \frac{h\nu_0}{g\beta} - \frac{hA_0}{g\beta} - \frac{1}{2}\frac{hA_0^2}{g\beta\nu_0}, \tag{3}$$

$$H_{e'} = \frac{h\nu_0}{g\beta} - \frac{hA_0^2}{g\beta}, \tag{4}$$

$$H_{e''} = \frac{h\nu_0}{g\beta}, \tag{5}$$

$$H_m = \frac{h\nu_0}{g\beta} + \frac{hA_0}{g\beta} - \frac{1}{2}\frac{hA_0^2}{g\beta\nu_0}, \tag{6}$$

where A_0 is the HF constant, ν_0 the microwave frequency. The correction due to HF interaction leads to a smaller g-factor ($g = 2.0026 \mp 0.0003$). The SHF interactions have clearly measurable influence on the centres of the SHF line groups also. The g-correction due to SHF interaction have been made in [10] for F-centres. For this correction it is necessary to know the effective coupling constants, which may be obtained from ENDOR measurements. However, the rough correction may be obtained and gave the value $g \approx -5 \times 10^{-4}$. Therefore, the SHF corrected g-factor of the $(H_2^-)_a$-centre ($g = 2.0021$) is about the same as that of the F-centre in LiF.

4. Summary

In most crystals of alkali halides the H_i^0-centres become mobile above 100 K and may be trapped by the other nonradiative defects. In alkali halides, doped with OH$^-$ ions the interaction between mobile H_i^0-centre and OH$^-$-ion leads to creation of the $(H_2O^-)_a$-centre. This centre is much better described as an F-centre with an embedded water molecule (which is chemically equivalent to H_2O^- in anion site). The ESR spectrum of the $(H_2O^-)_a$-centre is similar to that of the F-centre [5] and exhibits a

single broad band. In optical absorption a number of bands in the region of the F-absorption have been observed. The HF interaction with H$_2$O$^-$ protons A_0(H$_2$O$^-$) = = 34.5 MHz is very small compared to that of the free hydrogen atom A_0(H^0) = = 1420 MHz.

This is in strong contrast to the case of the chemically analogous H$_2$S$^-$-centre in KCl crystals [6], where the molecule–ion character of the centre results in more than 20 times smaller SHF interaction with its nearest neighbours (A(^{39}K) $<$ 1.3 MHz extracted from the inhomogeneous linewidth) and a large proton HF interaction A_0(H$_2$S$^-$) = 85.5 MHz. In contrast to the (H$_2$O$^-$)$_a$-centre, the ESR spectrum of the (H$_2$S)$_a$-centre exhibits the resolved HF structure.

The HF interaction with (H$_2^-$) protons A_0(H$_2^-$) = 646.5 MHz in LiF crystals is very large compared to that of the H$_2$O$^-$ and H$_2$S$^-$-centres. However, the SHF interaction with nearest neighbours is large also and a(Li) is only in two times smaller than a(Li) for F-centres in LiF (Table 1). Therefore, this centre has molecule–ion as well as F-centre character.

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