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$H_{s,c}^0$ -Centres in $LiF-H^-$, Mg^{2+}

By

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The ESR spectrum of an unperturbed hydrogen atom on a cation site is observed after vacuum-ultraviolet irradiation of $LiF-H^-$, Mg^{2+} crystals at room temperature. A production mechanism involving optical destruction of magnesium–vacancy dipoles and U-centres, release of the cation vacancies from the radiation-induced Mg-related centres, and subsequent capture of hydrogen atoms by the free cation vacancies, is proposed.

В кристаллах $LiF-H^-$, Mg^{2+} после облучения светом из области вакуумного ультрафиолета наблюдается спектр ЭПР невозмущенных атомарных центров водорода, находящихся в катионном узле. Предложен механизм образования этих центров, включающий оптическое разрушение магниевых диполей и U-центров, отход катионной вакансии от образованных магниевых центров и последующий захват этими вакансиями атома водорода.

1. Introduction

Atomic hydrogen can be trapped at substitutional cation sites in alkali halides additionally doped with divalent cations [1, 2]. It was shown by Hoentzsch and Spaeth [1] and Studzinski et al. [2] that the introduction of divalent cations like Ca^{2+} or Sr^{2+} produces in $KCl-OH^-$ and $RbCl-OH^-$ $H_{s,c}^0$ -centres perturbed by the impurity because the impurity–vacancy dipoles remain unaffected by irradiation.

In our previous paper [3] we have reported the results of investigations of $LiF-H^-$, Mg^{2+} crystals after X-irradiation at 80 K and subsequent heating to room temperature and above. Two types of atomic hydrogen centres connected with magnesium–vacancy dipoles were observed.

This paper reports the results of further investigations of atomic hydrogen centres in $LiF-H^-$, Mg^{2+} crystals.

2. Experimental Technique

The experimental technique and the preparation of the crystals have been described elsewhere [3, 4]. The $LiF-H^-$, Mg^{2+} crystals used in this work did not contain more than $3 \times 10^{17} \text{ cm}^{-3}$ U-centres (the intensity of the U absorption band at 9.7 eV is less than 100 cm^{-1} [4, 5]). The concentration of MgF_2 ranged from 0.05 to 0.1 wt% in the melt. Optical bleaching of the crystals was accomplished by unfiltered light of a VMF-25 hydrogen lamp with a MgF_2 window (maximum energy obtainable was 10.8 eV). In some cases, the crystals were irradiated by X-rays from a Pd tube operating at 40 kV and 50 mA.

Samples were quenched before VUV irradiation by heating them at 600 °C for 30 min and dropping them onto a metal block at room temperature.

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3. Results

Before optical treatment the absorption spectrum of LiF-H^- , Mg^{2+} or LiF-H^- crystals exhibits only the U absorption band with a peak at about 9.7 eV [4, 5] (Fig. 1). Optical destruction of U-centres leads to the formation of the F-band with a peak at 5.0 eV and centres having an absorption band at about 11 eV. No F absorption band arises by the same optical bleaching of "pure" LiF because the energy of light (10.8 eV) is too low for creation of free excitons in these crystals. At room temperature in the crystals doped with hydrogen, VUV light produces a conversion of U-centres into F-centres and interstitial hydrogen molecules, which are not detectable optically or magnetically.

At present, there are two different opinions on the nature of the absorption band at 11 eV. According to one of them, it is an exciton perturbed by an F-centre (β -band) [7, 8] and according to the other, it is a molecular halogen (V_3 -centre) [9, 10]. Both models are consistent with the experimental fact that the intensity of the band at about 11 eV increases linearly with the F-centre concentration in the pure crystals. Since after such treatment for formation of V_3 -centres is not expected, it may therefore be concluded that the absorption band at 11 eV in pure and hydrogen-doped LiF crystal is due to β -centres.

Optical irradiation of the Mg-doped LiF-H^- crystals produces two similar bands, and in addition, Mg-related absorption bands at 3.2 and 4.0 eV [11] and a broad band at about 9.0 eV (Fig. 1). One notes that, in LiF-H^- at 295 K, the β -band is about half as high as the F-band and the same ratio of the intensities was found in the pure crystal after X-irradiation [8] or VUV optical bleaching [9], whereas in the Mg-doped crystal the height of the absorption band at 11 eV is noticeably higher [9] (Fig. 1). Furthermore, the absorption bands at 3.2, 4.0, and 11 eV without the F-band [10] were observed in LiF-Mg crystals

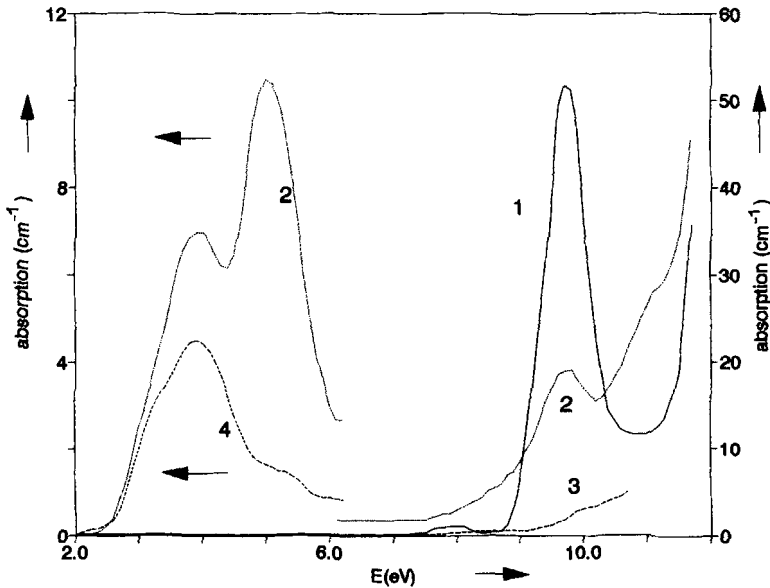


Fig. 1. Absorption spectra of (1), (2) LiF-H^- , Mg^{2+} and (3), (4) LiF-Mg^{2+} at 295 K, (1), (3) before and (2), (4) after vacuum-UV bleaching at 295 K

after X-irradiation at 80 K. These results suggest that the absorption band at about 11 eV produced in the Mg-doped crystals by X-irradiation or VUV bleaching is not associated with the β -band and is due to impurity doping, but in this paper we will not discuss the nature of this band at 11 eV in Mg-doped crystals.

As shown in Fig. 1, curve 4, the magnesium-related bands at 3.2 and 4.0 eV appear after the same optical bleaching in LiF-Mg crystals not additionally doped with hydrogen; in addition, a weaker Mg-related band at 5.5 eV [11], which is hidden under the F-absorption band in LiF-H⁻, Mg²⁺, can be observed.

It may be suggested that under VUV optical bleaching the transformation of magnesium-vacancy dipoles and the destruction of U-centres occur simultaneously. The formation of the magnesium-related centres having absorption bands at 3.2 and 4.0 eV is presumably due to the nonradiative annihilation of the self-trapped exciton near the magnesium-vacancy dipole. Some similar results related to the decay of the self-trapped exciton near an impurity have been reported earlier by us for NaCl-Mg [12]. It should be noticed that the energy for the creation of an exciton near an impurity may be sufficiently smaller than that of the free exciton.

The VUV bleaching of higher hydride-doped LiF-H⁻, Mg²⁺ crystals (above 10^{17} cm⁻³) leads to the formation of only F-centres because of the strong U-centre absorption, whereas X-irradiation produces also the Mg-related centres.

Fig. 2 shows the ESR spectrum of atomic hydrogen centres obtained by vacuum-UV irradiation of LiF-H⁻, Mg²⁺ for 2 h with a hydrogen lamp with a MgF₂ window at room temperature. It contains two groups of lines with a splitting of $(531 \pm 2) \times 10^{-4}$ T which is due to the hyperfine (HF) interaction of the unpaired electron with the proton. The simplest structure is observed for $\mathbf{B} \parallel \langle 111 \rangle$. Each of the groups of the spectrum measured with $\mathbf{B} \parallel \langle 111 \rangle$ exhibits a well-resolved structure consisting of seven equally spaced $((92 \pm 1) \times 10^{-4}$ T) lines. This indicates a superhyperfine (SHF) interaction with six equivalent fluorine nuclei. Observation of the same SHF structure in crystals enriched in ⁶Li confirms that the ESR spectrum resolves only the SHF interaction with the fluorine nuclei. It is therefore possible to assume that the observed centre is a hydrogen atom trapped at a free cation vacancy.

The analysis of the spectrum taking into account the Breit-Rabi correction [6] yields $g = 2.0034$ and a proton HF constant of $A = 1480$ MHz. Values of the parameters of the ESR spectra for this centre are given in Table 1. The value of the g -factor is given without the second-order correction due to the SHF interaction which leads to a smaller g -factor. Since the SHF interaction of the centre is large, the SHF correction gave the considerable value of $\Delta g = -23 \times 10^{-4}$ and the g -factor becomes considerably smaller than that of the free electron. Within the uncertainty of the experiment, the g -factor is isotropic.

Since the hydrogen atom in the cation vacancy is in the environment of six ¹⁹F ions and is not perturbed by the impurity, as it was observed in earlier works for KCl and RbCl

Table 1
Proton HF constants a_p , the g -factor, isotropic a_F and anisotropic b_F SHF constants

| g | a_p (10^{-4} T) | a_F (10^{-4} T) | b_F (10^{-4} T) |
|---------------------|-------------------------|-------------------------|-------------------------|
| 2.0034 ± 0.0003 | 531 ± 2 | 89 ± 1 | 16 ± 1 |

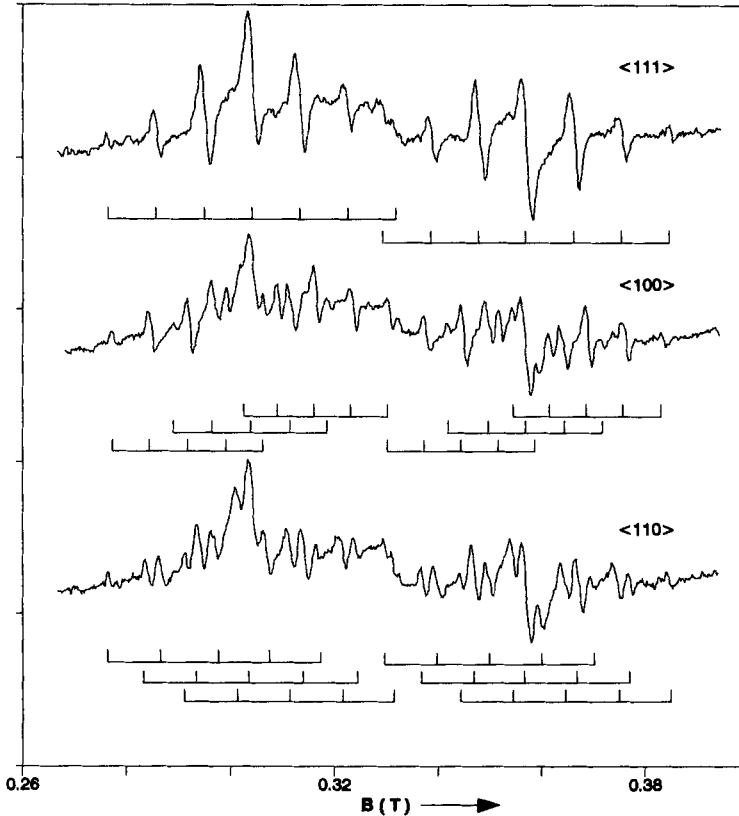


Fig. 2. ESR spectra of $H_{s,c}^0$ -centres in $LiF-H^{-}, Mg^{2+}$. $T = 295$ K, $\nu = 9376$ MHz

doped with Ca^{2+} or Sr^{2+} [1, 2] and $LiF-H^{-}, Mg^{2+}$ [3], we came to the conclusion that optical destruction of the magnesium–vacancy dipoles involves the formation of magnesium centres with absorption bands at 3.2 and 4.0 eV and the release of the cation vacancy in which the hydrogen atom can be trapped. This conclusion is supported by the fact that the $H_{s,c}^0$ -centres cannot be produced by VUV irradiation in the higher hydride-doped crystals in which the Mg-related absorption bands are not observed.

However, the centres are formed in the highly hydrogen-doped $LiF-H^{-}, Mg^{2+}$ crystals due to X-irradiation at 295 K, but not 80 K and subsequent heating to room temperature (the latter case has been considered in the previous paper [3]). In room temperature X-irradiated crystals of $LiF-H^{-}, Mg^{2+}$ in addition to the $H_{s,c}^0$ -centre ESR signal, ESR signals appear now due to a large number of F^{-} , H_2^{-} [13], and $H_i^0(Mg)$ -centres [3]. As a result, some of the lines of the $H_{s,c}^0$ -centre are hidden under the spectra of these centres and only the outer lines can be observed.

On decreasing the temperature to 80 K the spectrum of the $H_{s,c}^0$ -centre entirely disappears and one observes only a doublet ESR spectrum without resolved SHF structure (not shown in Fig. 2), which may be hidden under the spectrum of the $H_{s,c}^0$ -centre at room temperature. A similar doublet ESR spectrum is observed after thermal destruction of the $H_{s,c}^0$ -centres. It is possible that the observed doublet belongs to hydrogen atom centres, which were

studied in the previous work [3], but because of the small intensity of this signal it was difficult to identify it. When the temperature is raised again to 295 K the spectrum of Fig. 2 is fully restored. The nature of this disappearance of the spectrum upon lowering the temperature is not clear. It is conceivable that this is a saturation effect, but we have not been able to detect the spectrum at 80 K upon lowering a microwave power.

The $H_{s,c}^0$ -centres are unstable at room temperature, their half-life is of the order of three days. We have not been able to detect any absorption due to these centres in the range 2.0 to 11 eV. Optical bleaching with light of 3.2 to 4.5 eV at 295 K leads to a transformation of the Mg-related absorption bands, but not to a change of the ESR spectrum. This also indicates that the $H_{s,c}^0$ -centre is not associated with the magnesium-related bands at 3.2 and 4.0 eV. An unknown absorption band at about 9.0 eV appeared after VUV irradiation (Fig. 1) which decays above 200 °C and could therefore not be associated with the $H_{s,c}^0$ -centres.

In conclusion it should be noticed that in γ -irradiated LiF-OH⁻ crystals Akhvediani et al. [14] have observed the ESR spectrum of a hydrogen atom with partly resolved SHF structure consisting of seven lines for $\mathbf{B} \parallel \langle 111 \rangle$ and with SHF splittings between lines of 18×10^{-4} T. They have attributed it to the unperturbed hydrogen atom in a cation vacancy. However, the SHF structure is resolved only for $\mathbf{B} \parallel \langle 111 \rangle$ and this is not sufficient for a correct conclusion. 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. In a future paper we plan to explain this ESR spectrum on the basis of another model of the centre. This work is being carried on.

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