



# Optical functions and time-resolved luminescence of lithium hydride single crystals upon far-ultraviolet excitation



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## ABSTRACT

Low-temperature reflection spectra of lithium hydride (LiH) single crystals cleaved in ultrahigh vacuum ( $3 \times 10^{-10}$  Torr,  $T = 10$  K), were recorded using synchrotron radiation in vacuum ultraviolet spectral region. Based on the obtained experimental data, the optical functions of LiH in the energy range from 3.7 to 35 eV were analyzed using the Kramers–Krönig relations. Time-resolved photoluminescence excitation spectra were studied in detail for the near edge free exciton-phonon luminescence at 4.67 eV and photoluminescence at 2.4 eV due to the  $\text{Bi}^{3+}$  impurity centers. The effect of multiplication of electronic excitations due to inelastic scattering of hot photoelectrons and hot photoholes was revealed at photon energies above 15 eV (more than  $3E_g$ ). It was found that the radiative lifetime for free excitons in LiH at 4.67 eV is less than 1 ns as low temperatures as at 10 K. The interpretation of the electronic band structure of lithium hydride in the ultraviolet and vacuum ultraviolet spectral regions were carried out on the basis of the present experimental results with the involvement of the available band structure calculations.

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## 1. Introduction

Lithium hydride crystals possess crystal lattice of NaCl structure type (space group  $O_h^5$ ). The possible simplest electronic structure of  $\text{Li}^+$  and  $\text{H}^-$  ions, both having  $1s^2$  configuration, positions LiH specially among the numerous binary alkaline crystals and in many aspects it serves as an ideal model system for other ionic compounds [1]. However, the investigation of electronic excitation (EE) in LiH crystals is a complicated task due to its inherent high chemical reactivity. As a result LiOH,  $\text{Li}_2\text{CO}_3$  and other compounds can be formed in the crystal volume and on the surface if vacuum conditions are not sufficiently high in the experimental environment. These circumstances lead to the experimental data for LiH with considerable distortion of the measured optical properties. This is the reason that even such general characteristics as the reflection spectra in the wide vacuum ultraviolet (VUV) range remain studied with insufficient quality and therefore controversial results were revealed up to now. ‘True’ results in the VUV spectral region can be obtained only either by cleaving the LiH crystals in pure liquid helium at 4.2 K or under ultrahigh vacuum conditions both preventing surface contamination by reducing influence of ambient atmosphere. Such studies of reflection spectra in the

VUV region using synchrotron radiation (SR) have been earlier undertaken several times in an oil-free vacuum of  $1 \times 10^{-6}$  Torr at  $T = 295$  K [2] or even in high vacuum of  $1 \times 10^{-8}$  Torr at  $T = 5$  K [3]. However, the considerable changes in the reflection spectra as a function of time after the cleaving were observed in all these works. The degradation of the reflection spectra is especially significant in the VUV region of 7–15 eV [2–4]. Therefore, no true reflection spectra in ultrahigh vacuum have been unfortunately recorded and accordingly no reliable spectra of optical functions have been calculated for LiH crystal so far. However, a recent brief communication [5] has reported a mirror reflection spectra recorded using synchrotron radiation for LiH and LiD single crystals, which were cleaved in ultrahigh vacuum  $2.8 \times 10^{-10}$  Torr at  $T = 8$  K. This spectrum comprises a prominent structure located in the excitonic energy region. The reflection coefficient in the VUV energy region was high in magnitude and did not change during the observation period. The author [5] (co-author of the current publication) suggests that it is a true reflection spectrum of lithium hydride in the VUV energy region, and it can serve as a basis to calculate the spectra of the optical functions and to determine the electronic structure of the model object.

The aim of the present work is to study the reflection spectra, to analyze the deduced optical functions together with the photoluminescence excitation spectra of free exciton and impurity  $\text{Bi}^{3+}$ -center emissions in LiH crystals, cleaved in ultrahigh vacuum at low temperatures.

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## 2. Experimental details and samples

The experiments were performed at the SUPERLUMI station (beamline I) of HASYLAB at DESY (Hamburg, Germany) [6]. The Al and Pt coated gratings of the primary monochromator were applied in measurements covering spectral range from 4 to 35 eV. The photoluminescence (PL) in visible and ultraviolet (UV) spectral regions was analyzed by means of a 0.5 m Czerny–Turner mounting B&M monochromator equipped with a photomultiplier tube XP20200Q (Valvo) operating in the time correlated single photon counting mode. Time-resolved PL emission spectra and time-resolved PL excitation (PLE) spectra were recorded within a time window (TW) of length  $\Delta t$  correlated with the arrival of SR-pulses (delayed  $\delta t$ ). In the present experiments the delay and length of  $\delta t_1 = 1.9$  ns,  $\Delta t_1 = 8.5$  ns (TW<sub>1</sub>), and  $\delta t_2 = 19.5$  ns,  $\Delta t_2 = 158$  ns (TW<sub>2</sub>) were used. The excitation pulses from the DORIS storage ring had a FWHM of 130 ps and a repetition period of 192 ns. The time resolution of the entire detection system was 1 ns (FWHM). The PL excitation spectra were corrected to an equal number of photons incident on the sample using sodium salicylate. The LiH samples, mounted onto the sample holder attached to the cold finger of the cryostat, were cleaved directly before measurements in ultrahigh vacuum of  $3 \times 10^{-10}$  Torr at temperatures 7–10 K. The reflection spectra were recorded simultaneously with time-resolved PL excitation spectra at the incidence angle of  $17.5^\circ$  immediately after cleaving of the crystal. The spectral resolution of the primary monochromator was as high as 0.18 nm.

The LiH single crystals were grown by one of the authors (V.A.P.) at Ural Federal University (Yekaterinburg, Russia) using a modified Czochralski method. Crystal growth process has been described in detail in [4]. A lithium metal distilled in vacuum, and spectroscopic quality hydrogen H<sub>2</sub> were used as starting materials during the growth process. The crystals were grown in the form of the cylinders with the length of 6–8 cm and the diameter of 2–3 cm. As grown samples were slightly blue-colored due to the colloidal lithium particles, therefore the crystals were annealed in hydrogen at 550 °C to reduce an internal tension and improve stoichiometry. The amount of the metal impurities in the crystals was lower than  $10^{-4}$  mol%, the content of O<sub>2</sub> and N<sub>2</sub> impurities was less than  $10^{-3}$  mol%. Before installing samples to a cryostat, the smaller pieces with dimensions of  $\sim 8 \times 5 \times 4$  mm<sup>3</sup> were cleaved from the crystal boule in dry hot air and mounted to the specially developed device for crystal cleavage. The samples were oriented in the [100] plane. Up to three samples simultaneously can be mounted on the crystal holder. Analogously designed cleaving device has been successfully used earlier in VUV studies of highly hygroscopic CaO [7] and SrO [8] crystals at MAX-Lab, Lund Sweden.

Reflection spectra were analyzed using the Kramers–Krönig transform [9] to calculate the dispersions of the optical functions. The reflection spectra were initially recorded in arbitrary units. A normalization procedure was performed to calculate the absolute values of the reflection coefficient  $R(E)$  using the refractive index spectra for the transparency region of the LiH crystal where the refraction index  $n(E)$  is known:  $n = 2.02$  at  $E = 2.54$  eV [1].

## 3. Experimental results and discussion

### 3.1. Dispersions of the optical functions and electronic structure of LiH crystals

Fig. 1 shows the reflection spectra at  $T = 10$  K recorded for both the pristine and cleaved LiH crystals. Fig. 1 reveals that the most significant changes in  $R(E)$  spectra are observed at photon energies above 6 eV, i.e. in the region of interband transitions. The features

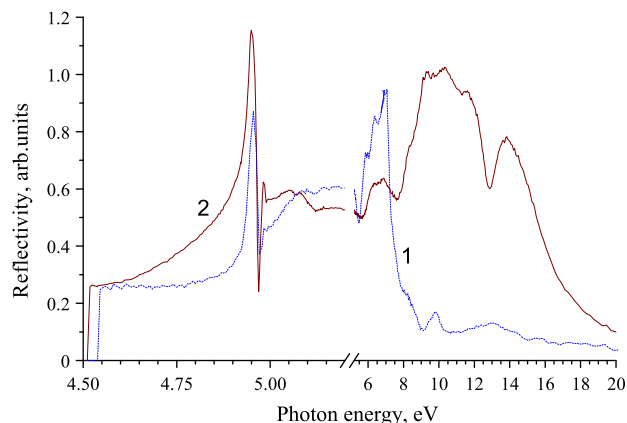


Fig. 1. The reflection spectra of LiH single crystals at  $T = 10$  K recorded for both pristine (1) and cleaved at  $T = 10$  K (2) crystals. The  $R(E)$  coefficient is specified in arbitrary units. Both spectra are normalized in intensity at  $E = 4.5$  eV.

in the spectra above 8 eV are practically absent for pristine crystal, which shows that surface reaction with atmospheric gases taking place during the sample mounting disturb reflection spectra significantly. Fig. 2 (curve 1) demonstrates the time evolution of reflection spectra during the whole experimental cycle. The cleavage of the LiH single crystal was performed at  $T = 10$  K in vacuum of  $3 \times 10^{-10}$  Torr without a change of the ambient pressure in the ultra-high-vacuum chamber. It is significant that the reflection spectrum recorded immediately after cleavage (Fig. 2, curve 1) did not change over a long time (continuous monitoring was carried out  $\sim 3.0$  h). This fact indicates that experimental vacuum conditions were well suited to keep the highest purity of the cleaved surface. Only much longer intentional storage of a cleaved crystal in vacuum led to some changes in the reflection spectrum. Fig. 2 (curve 2) shows that a cleaved crystal stored for 20 h, even in a vacuum better than  $10^{-9}$  Torr, undergoes some distortions in the reflection spectrum in the VUV-energy region. This is particularly evident at energies above 9 eV, however all major features are present as Fig. 2 testifies. From these results it follows firstly that the LiH reflection spectra for the VUV energy range, previously presented in Refs. [2,3], cannot be considered to be trustworthy. Secondly, the changes in the reflection spectrum after the cleavage, which was observed in Ref. [3] are not associated with the formation of lattice defects at the surface layers of LiH crystal under the

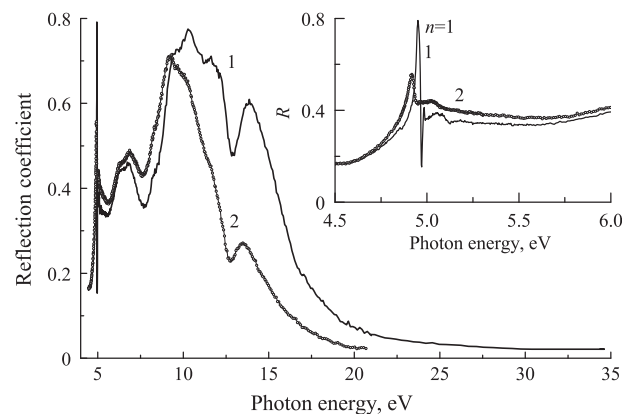


Fig. 2. The reflection spectra of LiH single crystals recorded at  $T = 10$  (1) and 270 K (2). The crystal was cleaved at  $T = 10$  K in vacuum of  $3 \times 10^{-10}$  Torr. The spectrum (1) was recorded immediately, and the spectrum (2) was recorded after 20 h storage in vacuum of  $2.5 \times 10^{-9}$  Torr. The inset shows the fragment of the reflection spectra for the energy region of fundamental absorption edge.

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