

Comparison of the isotope, pressure, and temperature shifts in the excitonic spectra of LiH and LiD crystals

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It has been established experimentally for the first time that the isotope and temperature shifts of the excitonic levels in LiH and LiD crystals are not determined by the change in the crystal lattice spacing but instead primarily by the exciton-phonon interaction.

Lithium hydride is a remarkable and highly promising material both from the scientific and applied points of view.¹ In particular, it is a system that exhibits the largest conceivable isotopic effects when hydrogen is replaced by deuterium and tritium isotopes.

Lithium hydride has a NaCl-type lattice and is built up of Li^+ and H^- ions with the same electronic configuration $1S^2$. Near the edge of the fundamental absorption of LiH and LiD, which is caused by direct interband transitions $X_1 \rightarrow X'_4$, the reflection spectra exhibit at $T < 100$ K and the E_1 and E_2 lines which are attributed to the first terms of the excitonic series.¹ Upon the transition from LiH to LiD, these lines undergo an enormous short-wave isotope shift, ~ 95 and ~ 100 meV for E_1 and E_2 , respectively. What causes the isotopic effects of this magnitude? Is it the smaller lattice constant or the change in the exciton-phonon interaction? Experiments on hydrostatic compression, which can be used to smoothly change the interatomic distances in the

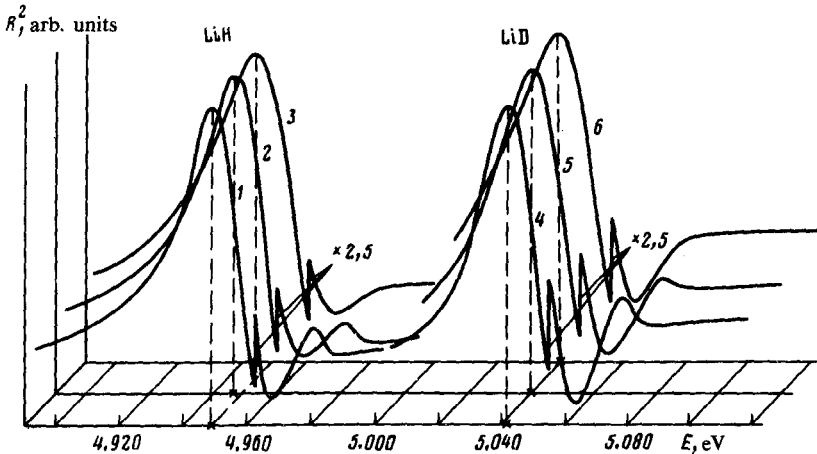


FIG. 1. The spectrum of double reflection of LiH and LiD crystals at a temperature of 77 K and at various pressures. LiH: 1—1 bar; 2—5.1 bar; 3—11.7 kbar; LiD: 4—1 bar; 5—8.6 bar; 6—12.0 kbar.

crystal, can provide an answer to this question. In the present letter we report a study of the effect of pressure up to 13 kbar at 77 K and the E_1 and E_2 lines in the reflection spectra of LiH and LiD crystals.

The LiH and LiD single crystals, which were grown from a melt by Stockbarger's method, were subjected to a prolonged annealing in H_2 or D_2 . To avoid oxidation of the surface, we cleaved the crystals and inserted them into a high-pressure chamber in dry argon. The crystals were compressed in a high-pressure apparatus² which consisted of a 15-kbar helium compressor, an optical chamber with two leucosapphire windows, and a nitrogen cryostat. We measured the spectra of double reflection of light at a 45° angle from two freshly cleaved crystals which were placed in a special holder. We used a LD deuterium lamp, a MDR-23 diffraction monochromator (with a dispersion of $13 \text{ \AA}/\text{mm}$), and a FEU-106 photomultiplier with a photon-counting system.

Figure 1 shows the reflection spectra of LiH and LiD at different pressures, and Fig. 2 shows the pressure dependence of the position of the maxima of the E_1 and E_2 lines. We see that the E_1 line describes a small long-wave shift and the E_2 line shifts very slightly. As a result, the energy spacing $E_2 - E_1$ increases with the pressure. The shift rates dE_1/dP and dE_2/dP , which are determined from the set of experimental points (Fig. 2) with use of the linear regression, are, respectively, -0.30 ± 0.02^2 and $0.02 \pm 0.05 \text{ meV/kbar}$ for LiH and -0.48 ± 0.02 and $0.01 \pm 0.03 \text{ meV/kbar}$ for LiD. The intensity of the E_2 line decreases with increasing pressure and at 9–11 kbar it virtually disappears. The shifts of the two lines are reversible with the pressure.

Knowing the pressure coefficients dE_1/dP and dE_2/dP for the E_1 and E_2 lines, we can determine the hydrostatic deformation potentials for the corresponding excitonic transitions from the relation $E_d = dE/d \ln V = -(1/\kappa_T)(dE/dP)$, where κ_T is the isothermal compressibility of the crystal. Using the value $\kappa_T = 3 \times 10^{-6} \text{ bar}^{-1}$ for LiH, which was calculated⁶ from the elastic constants at 77 K, and assuming that the

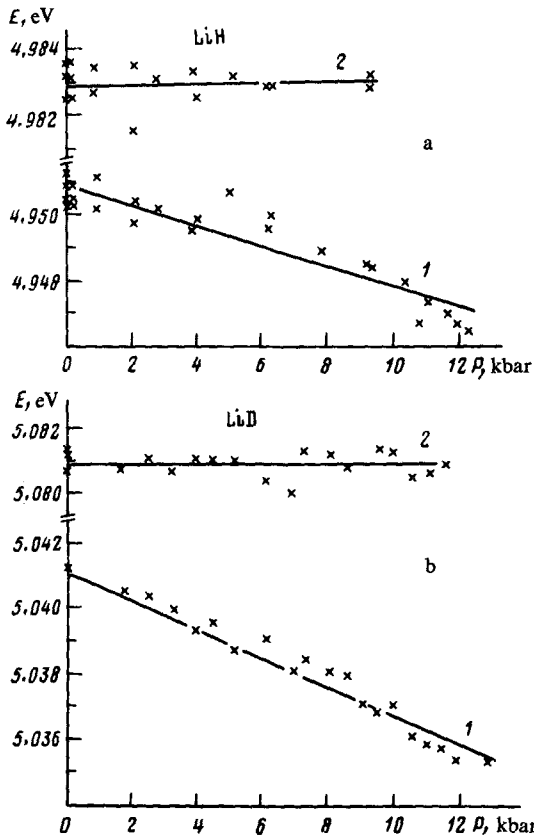


FIG. 2. Pressure dependence of the position of the maxima of the E_1 and E_2 exciton reflection lines for LiH (a) and LiD (b) crystals at $T = 77$ K. 1—Shift of the E_1 line; 2—shift of the E_2 line.

value of κ_T is the same for LiD, we find the following values of E_d for the excitonic transitions under consideration: 0.10 and ~ 0 eV for LiH and 0.16 and ~ 0 eV for LiD.

At $T = 77$ K and $P = 1$ bar, as we go from LiH to LiD, the lattice constant a decreases⁷ by 0.016 Å. If the compressibility of LiH is taken into account, the lattice constant a will change by the same amount at $P = 3.94$ kbar. According to our data, however, a 3.94-kbar pressure shifts the E_1 and E_2 lines in LiH by only -1.2 and 0.1 meV, which amounts to no more than 1.5% of the isotope shift. This circumstance shows conclusively that the isotope line shift cannot be attributed to a decrease in the lattice constant and is determined principally by the exciton-photon interaction, more exactly, by the interaction of an exciton with the LO phonons, since the frequency ω_{LO} of LiH differs markedly from the frequency ω_{LO} of LiD (these frequencies are⁸ 1120 and 880 cm^{-1} , respectively).

The high energy of the exciton-phonon interaction and the increase in the spacing between the E_1 and E_2 lines with increasing pressure and with a simultaneous decrease in the intensity of the E_2 line (the last effect shows that the ionization energy of the excitonic E_2 level decreases because of its approach to the electron-hole continuum)

suggest that a simple hydrogenlike model of the Mott-Wannier exciton cannot be used to exactly describe the excitonic states in LiH and LiD crystals.

Aside from the pressure-induced shifts, we have also measured temperature-induced shifts of the E_1 and E_2 lines in the temperature range 4.2–300 K. With the increase in temperature, the lines shift toward the long-wave side. The intensity of the E_2 line decreases gradually (as it does when pressure is applied) and the line vanishes near 150 K as a result of thermal ionization of the excitonic state. The temperature coefficients $(dE_1/dT)_p$ and $(dE_2/dT)_p$ of LiH near 77 K are approximately -0.05 and -0.08 meV/K, respectively. A comparison of the pressure and temperature-induced shifts for LiH on the basis of the relation $(dE/dT)_p = (\partial E/\partial T)_V - (3\alpha/\kappa_T)(\partial E/\partial P)_T$, where the first term is due to the exciton-phonon interaction, and the second term is due to the thermal expansion of the lattice ($\alpha = 5.6 \times 10^{-6} \text{ K}^{-1}$ is the linear thermal expansion coefficient of LiH at⁷ 77 K) shows that at 77 K the dominant contribution ($> 98\%$) to the temperature-induced shift of the E_1 and E_2 exciton lines is the exciton-phonon interaction, rather than the thermal expansion of the crystal. A similar situation occurs in LiD.

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²In the case of LiH, Kondo and Asaumi³ have observed a long-wave shift of the E_1 line at an average rate of nearly -1.1 meV/kbar over the pressure range 80–330 kbar at a temperature of 300 K. The theoretical calculations of the band structure of LiH at pressures of 0 and ~ 2 Mbar carried out by Perrot⁴ show that the direct gap $X'_4 - X_1$ decreases at an average rate of -0.17 rydbergs/2 Mbar or -1.2 meV/kbar. According to Kulikov's⁵ calculations, in LiH this gap varies only slightly at relatively low pressures and then gradually decreases down to zero at ~ 2 –3 Mbar.

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Translated by S. J. Amoretty