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### Isotopic and disorder effects in large exciton spectroscopy

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<u>Abstract.</u> Most of the physical properties of a solid depend to a greater or lesser degree on its isotopic composition. For the first time a systematic analysis is presented of isotopic and disorder effects observed in crystals of various isotopic composition using low temperature large exciton spectroscopy. Substituting a light isotope with a heavy one increases the interband transition energy and the binding energy of the Wannier – Mott exciton as well as the magnitude of the longitudinal-transverse splitting. The nonlinear variation of these quantities with the isotope concentration is due to the isotopic disordering of the crystal lattice and is consistent with the concentration dependence of line halfwidths in exciton reflection and luminescence spectra. The common nature of the isotopic and disorder effects in the crystals of C, LiH, CdS, Cu<sub>2</sub>O, and Si and Ge is emphasized.

#### 1. Introduction

It has been traditionally assumed that the main application of lithium hydride is in nuclear power engineering. This view, however, has changed considerably over the past thirty years. Lithium hydride is now also regarded as a promising material for high-temperature superconductors [1], this property being attributed to the conduction band of the metallic hydrogen [2]. The discovery of line luminescence of free excitons,

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observed over a broad temperature range [3], has placed lithium hydride among the tentative sources of coherent UV radiation [4]. Apart from these recognized applications, numerous new possibilities have opened up recently in connection with rapid advances in the physics of solids with isotopic compositions (diamond, lithium hydride, zinc oxide, cadmium sulfide, germanium, etc.) - namely, isotopic engineering [7, 6]. For example, there are elements of fiber optics which take advantage of the different refractive indices of different isotopes; optical memory and information storage modules; all kinds of radiation detectors, the homogeneous doping of semiconductors through neutron transmutations; and many other practical applications (for more details see Refs [3, 6, 7]). The use of materials with specific isotopic compositions requires a comprehensive knowledge of the fundamental principles of the physics of electron and phonon states of the substances, since many applied problems are primarily related not only with the migration of energy, but also with the scattering of electron excitations by phonons. The most rewarding method of studying these processes may well be the method of exciton spectroscopy.

Now, almost six decades after the introduction of the exciton quasi-particle by Ya I Frenkel [8], the outstanding potency of this idea is especially clear. According to Frenkel, an exciton is the electron excitation of an atom (ion) in a lattice, which by virtue of the translational symmetry of the latter, migrates within the crystal as an electrically neutral formation. After Frenkel, the concept of an exciton was further developed by Peierls [9], Slater and Shockley [10]. A different approach to the problem of light absorption by a solid was developed by Wannier [11] and Mott [12]. According to Wannier and Mott, an exciton is a Coulomb-bound state of an electron and hole, which are considerably separated spatially, and whose charges are screened. Since

Frenkel dealt with excitons localized on the lattice site, in the wake of the Wannier-Mott studies it became usual to distinguish Frenkel excitons (small-radius excitons; see Ref. [13]), and Wannier-Mott excitons (large-radius excitons [14]). There is, however, no fundamental difference between these two models [13-15]. The experimental discovery of a large-radius exciton by E F Gross [16] in the hydrogen-like absorption spectrum of semiconductor crystals launched the new science of exciton physics (see also Refs [17, 18]). It has been demonstrated more than once (see Ref. [16] and references therein) that external factors (electric and magnetic fields, axial and hydrostatic deformation) affect the optical spectra of Wannier-Mott excitons and their energy characteristics (see also Ref. [19]). These studies have provided very accurate details concerning not only the binding energy of large-radius excitons, but also their translation mass, the effective masses of charge carriers, their g factors, etc. Moreover, a detailed study of photonexciton interactions has led to the concept of polaritons [20]. The problem of the interaction between excitons and the lattice [21] has remained topical for over four decades since the discovery of the Wannier-Mott exciton [16].

In the adiabatic approximation the dependence of the binding energy of an electron in a hydrogen atom on the nuclear mass is described by

$$Ryd = 2\pi^2 \frac{mc^4}{h^3 c(1 + m/M_{\rm H})},$$
(1)

where *m*,  $M_{\rm H}$  are the masses of the electron and the nucleus, respectively. In the Wannier–Mott model, the Schrödinger equation for the exciton is resolved into the function of a hydrogen-like atom whose effective mass is  $Z_e = e/\varepsilon$  ( $\varepsilon$  being the dielectric constant of the medium), and the energies of the exciton states are described by the hydrogen-like expression of the form (see, for example, Ref. [14])

$$E_n(k) = E_{\rm g} - \frac{\mu e^4}{2h^2 \varepsilon^2 n^2} + \frac{h^2 k^2}{2(m_{\rm e}^* + m_{\rm h}^*)}, \qquad (2)$$

where k is the quasi-momentum of the exciton;  $\mu$ , n are its reduced mass and principal quantum number, and the translation mass of the exciton (M) is equal to the sum of the effective masses of electron  $(m_e^*)$  and hole  $(m_h^*)$ . By analogy with Eqn (1), the binding energy of exciton  $E_{\rm b} = \mu e^4 / 2h^2 \varepsilon^2 n^2$  is practically independent of the nuclear mass. Hence we come to the natural conclusion that there is no isotopic effect in a frozen crystal lattice on the levels of the Wannier-Mott exciton. This simplified treatment, however, does not take into account the exciton – phonon interaction, which to a certain extent is non-adiabatic (see, for example, Ref. [22]). The constant of exciton-phonon interaction depends on the frequency of phonons, and hence on the mass of vibrating crystal-forming particles — that is, on the mass of the isotopes. The isotopic dependence of the binding energy of large-radius excitons was observed experimentally with LiH and LiD crystals in Ref. [23], where the reflection spectra of these crystals at low temperatures were measured for the first time (see also Ref. [24]). As will be shown below, the discovered dependence of  $E_{\rm b}$  on the isotopic composition of the lattice has opened unique opportunities not only for reconstructing experimentally the constants of the Coulomb and Frohlich interactions, but also for controlling the efficiency of the exciton – phonon (polariton-phonon) interaction.

The study of energy spectra of elementary excitations in condensed media with short-range interaction has a long history [25]. Although the kinetic phenomena in disordered media are often of the same nature as those in crystals (see, for example, Ref. [26]), the energy spectrum of elementary excitations in non-crystalline media is more complicated. For instance, in addition to the coherent states which conserve quasi-momentum, the non-crystalline media exhibit localized states. The proportion of the latter, given that the degree of disorder is high enough, can be quite considerable (in the one-dimensional case, for example, all states are localized), so that the localized states will substantially modify the kinetic behavior (see also Ref. [27]). The contemporary physics of disordered systems is a vast and diversified branch of the physics of condensed matter. In addition to the monographs cited above, we should also mention the reviews [28-30] concerned with the effects of varying degrees of disorder on the characteristics of electron excitations in such systems. Still, even though Ref. [30] gives a rather detailed analysis of the effects of disorder on the characteristics of free and bound excitons in chemically mixed crystals (mostly using the examples of A<sub>2</sub>B<sub>6</sub> and  $A_3B_5$ ), the effects of isotopic composition on the exciton states have not been considered. In this respect the present paper may be regarded as an addendum to the review [30] of the optical properties of chemically mixed crystals.

There were three main stimuli for the writing of this paper: firstly, a rather large bank of information on the spectroscopy of large-radius excitons in crystals where the isotopic effect is present has accumulated over the past twenty years, which has not yet been reflected in any major review. As will be shown below, these studies have started a new direction in the physics of large-radius excitons. The second stimulus is associated with the practical requirements of isotopic engineering (for more details see Refs [6, 7]). Finally, it is necessary to develop the Wannier – Mott theory itself (see, for example, Refs. [31-33]), which requires knowledge of the static and dynamic characteristics of large-radius excitons in different media under different conditions.

Our review consists of seven sections. It starts with the traditional introduction; Section 2 is concerned with the experimental studies of large-radius excitons in lithium hydride crystals. We also give a brief comparison of excitons in the crystals of C, ZnO, CdS, Ge and Cu<sub>2</sub>O in relating to isotopic effect. The band structure of LiH crystals, in comparison with the experimental results, is briefly described in Section 3. A more substantial fourth section considers the problems of the exciton-phonon (primarily Frohlich) interaction, and the isotopic effect on the electron (exciton) states. We demonstrate that the replacement of a light isotope with a heavy one leads not only to an increase in  $E_g$  (which has been known for LiH for almost fifty years [34]), but also to an increase in the binding energy  $E_{\rm b}$ . It ought to be noted that these effects (the change in  $E_{g}$  and  $E_{b}$ ) are most conspicuous in LiH crystals, although today they can also be reliably measured in other crystals with isotopic compositions. The results of experiments on exciton - phonon luminescence are described, which prove the existence of excitons quasimomentum in LiH crystals and their isotopic analogs, enabling one to monitor their band relaxation. Another interesting manifestation of the isotopic effect is the increase of the magnitude of longitudinal-transverse splitting of polaritons when a light isotope is replaced with a heavy one. These results are discussed in Section 5. Section 6 is devoted to

the effects of isotopic disorder on Wannier – Mott excitons in crystals with isotopic composition. The disordering of a crystal lattice creates not only a nonlinear dependence of  $E_g$ on the isotope concentration x, but also nonlinear line broadening with increasing x in the exciton spectra of reflection and luminescence in crystals of lithium hydride and germanium. Once again, these effects are strong enough to be easily registered with modern equipment for lowtemperature spectroscopy of large-radius excitons. In the Conclusions we discuss the difficult and yet unsolved problems in the physics of large-radius excitons in disordered media with isotopic composition. From the immense volume of literature concerned with excitons in disordered and isotopic media, we primarily selected those reviews and monographs which contain extensive bibliographies.

#### 2. Excitons in crystals of LiH

### 2.1 A comparative study of the edge of fundamental absorption in LiH, Li<sub>2</sub>O, LiOH, and Li<sub>2</sub>CO<sub>3</sub>

Let us briefly discuss the history of studies of the edge of fundamental absorption (reflection) of lithium hydride, which will allow us to proceed immediately to the point. Although the first measurements of absorption spectra in thin films of lithium hydride were carried out as early as the 1930s [34-36], the problem of the starting point of fundamental absorption of LiH remained controversial for a good forty years [37-41]. This was primarily due to the fact that the results of Rauch [36] were different from those of Refs [34, 35], and he attributed the absorption band observed in Refs [34, 35] around at 4.9 eV at room temperature to the absorption by F-sites (see also Ref. [41]). The main cause of major disparities between the results of different authors is the high hygroscopicity and the extremely high reactivity of lithium hydride. However, carefully prepared thin films of lithium hydride permitted Pretzel, together with colleagues [37] not only to reproduce the results of Refs [34, 35] with a high enough accuracy, but also to measure the absorption coefficient in the long-wave band (the exciton band with  $E_{\rm M} = 4.92$  eV at room temperature [5]), which was found to be of the order of  $10^5 \text{ cm}^{-1}$ . It was this that allowed the attribution of the long-wave band in the fundamental absorption spectrum of lithium hydride to the production of excitons in lithium hydride [39]. Notwithstanding the conclusive results of this study, for another fifteen years the opinion still prevailed (see, for example, Refs [39, 40]) that the edge of fundamental absorption lay in the vacuum UV range, in accordance with Rauch's results [36]. The confusion was aggravated by the lack of data on the edge of fundamental absorption of the compounds (Li<sub>2</sub>O, LiOH, etc.) likely to occur on the surface of LiH as a result of oxidation (for more details see Ref. [42]).

A breakthrough was made in studies [23, 24, 43-48]. Numerous measurements of the edge of fundamental absorption, performed with LiH crystals from different lots, demonstrated that the edge of absorption lies in the neighborhood of 5 eV (Fig. 1). Among the compounds listed in the heading of this section, LiH has the longest-wavelength edge of fundamental absorption. The closest to LiH is the edge of fundamental absorption of Li<sub>2</sub>O crystals [44] (see also Refs [47, 48]). According to Refs [49, 43, 45], absorption by crystals of LiOH and Li<sub>2</sub>CO<sub>3</sub> is shifted towards shorter wavelengths. All these compounds, with the apparent exception of LiOH



**Figure 1.** Absorption spectra of crystals: I - LiH [49];  $2 - \text{Li}_2\text{O}$  [44]; 3 - LiOH [49];  $4 - \text{Li}_2\text{CO}_3$  [45] at room temperature.

[49], exhibit direct electron transitions which shape the longwave edge of fundamental absorption. The edge of absorption of LiOH crystals shows a long tail [49], which may be attributed not only to indirect electron transitions, but also to the poor quality of these crystals [45]. The lack of detailed low-temperature spectroscopic data on the absorption (reflection) of these crystals currently prevents a more comprehensive interpretation. It ought to be added that the detailed investigations carried out in Ref. [50] indicate that what is primarily observed are the changes in the reflection spectrum of LiH crystals in the 6-15 eV range, which are due to photolysis rather than oxidation or hydration of the crystal surface.

The results quoted in this section indicate that the comparative study of the edge of fundamental absorption of LiH,  $Li_2O$ , LiOH and  $Li_2CO_3$  crystals gives evidence that lithium hydride exhibits the lowest energy of band-to-band transitions among these substances.

#### 2.2 Exciton reflection spectra of LiH crystals

At room temperature and normal pressure, lithium hydride forms a cubic lattice of NaCl type — that is, the crystal is built of two cubic face-centered lattices displaced with respect to each other by a half-period of the lattice [51]. Compounds with such a crystalline structure belong to the symmetry group  $O_{\rm h}^5$ . According the type of chemical bond, LiH is traditionally regarded as an ionic compound [alkalinehalide crystals  $A_1B_7$  (AHC)]. A more careful study of this problem, however, reveals that the heteropolarity ranges from 0.8 to 1 (see, for example, Ref. [52]). If we compare the radii of ions  $r_{\text{Li}^+} = 0.68 \text{ A}$  and  $r_{\text{H}^-} = 1.5 \text{ A}$  with the lattice constant l = 2.042 A, it becomes evident that crystals built of cations and anions of highly unequal size exhibit especially low melting temperatures [41]. According to Ref. [53], this feature is explained by the effect of double repulsion: the large ions are in contact not only with their closest neighbors, but also with one another. The main structural characteristics of lithium hydride (and its isotopic analogs) are given in Table 1 together with those of the AHC LiF, a typical representative of the A<sub>1</sub>B<sub>7</sub> family.

Specimens of LiH, LiD,  $\text{LiH}_x D_{1-x}$  (0 < x < 1) were grown from melt using the modified Bridgman–Stockbagger method (see also Ref. [54]). This technique is described in detail in Ref. [57]. To improve the stoichiometric composition

Parameter	LiH	LiD [37, 60-62]	LiT	LiF [63-65]
Lattice constant, A	4.084 40,65 (16 K)	4.068 4.0149 (16 K)	4.0633	4.017 4.001 (0 K)
Density, g cm $^{-3}$	0.775	0.802		2.640
Binding energy, kcal mol <sup>-1</sup>	-217.8	-218.8		-243.6
Heat of formation, kcal mol <sup>-1</sup>	-21.67	-21.78		-145.2
Melting point, K	961	964		1115
Refraction index	1.9847	1.9856		1.3916
$arepsilon_{\infty}$ $arepsilon_{0}$	$\begin{array}{c} 3.61 \\ 12.9 \pm 0.5 \end{array}$	$\begin{array}{c} 3.63\\ 14.0\pm0.5\end{array}$		1.96 9.01

Table 1. Main lattice parameters of LiH, LiD, LiT, and LiF crystals.

with respect to hydrogen (deuterium), the crystals grown were additionally annealed in an atmosphere of hydrogen or deuterium at a gage pressure of 3 to 5 atm and a temperature 500 to 550° C (melting point is 961 K and 964 K for LiH and LiD, respectively). For some crystals the time of heat treatment was as long as 20 days (for more details see Refs [41, 54]).

Given the high reactivity of freshly cleft LiH crystals in the atmosphere, we had to develop a procedure of cleaving which would not only ensure an initially clean surface, but also allow us to keep it fresh for a few hours (the time taken to complete an experiment). These requirements are satisfied by the wellknown method of cleaving directly in the helium chamber of the optical cryostat under liquid or superfluid helium, first tried in Ref. [55]. We did not notice any changes in the spectra of reflection [5], or luminescence [56], or resonant Raman light scattering (RRLS) [57] while working for 10 to 16 hours with the surface prepared in this way (see also Ref. [58]). The device for cleaving the crystals had three degrees of freedom and rotated through 90°, which greatly helped in carrying out the experiments. As a rule, specimens for experiments were cleft off bulky high-quality crystals. In addition to the chemical and mass-spectrometric analysis [49] of the concentration of anions (isotopes) in the solid solution  $LiH_xD_{1-x}$ , the composition of the crystals was also checked by measuring the location of the maximum of the no-phonon emission line of free excitons [59]. X-ray analysis indicates [60] that mixed crystals form a continuous series of solid solutions and behave as a virtual crystal with lattice constant changing according to Vegard's law. The experimental setup for measuring the low-temperature reflection and luminescence spectra has been described more than once (see, for example, Refs [55-58]) and consists of a double grating or prism monochromators, an immersion helium cryostat, and a photovoltaic detector (in photon counting mode). The results presented in this paper were obtained from a clean crystal surface cleft, as described above, directly in liquid helium. The spectra of mirror reflection were measured (if not indicated otherwise) using an the angle of incidence of 45°. For our studies we selected specimens which exhibited low dependence of exciton spectra of reflection and luminescence on surface features (see also Ref. [56]).

The spectrum of mirror reflection of LiH crystal with a clean surface<sup>†</sup> at T = 4.2 K is plotted in Fig. 2. We see that the spectrum exhibits a well-developed fine structure. The longwave reflection maximum corresponds to an energy of  $E_{1s} = 4.950$  eV. This maximum shows a conspicuous singularity on the short-wave side at 4.960 eV [57]. A similar pattern in the reflection spectrum of a clean crystal surface was repeatedly observed later (see, for example, Ref. [50]). Towards the shorter wavelengths away from this band, the dispersion dip is followed by another maximum at  $E_{2s} = 4.982$  eV. As the temperature increases, this peak shifts towards the longer wavelengths and its intensity decreases (Fig. 3); at  $T \leq 115$  K it becomes indiscernible (Fig. 4). This allows one to believe that the falling intensity of the  $E_{2s}$  peak is due to the process of ionization of the states responsible for this maximum. By analogy with the results of Ref. [66], the ionization energy of this state can be roughly estimated assuming that  $\Delta E_{2s} = k_{\rm B}T$  (where  $k_{\rm B}$  is the Boltzmann constant). According to such an estimate, the ionization energy is  $\Delta E_{2s} \cong 10$  meV. It ought to be added that the longwave drift of this state with increasing temperature is not the same as the shift rate of the long-wave reflection band (see below). The high values of the reflection coefficient (0.7-0.9)of the first long-wave peak, and its relatively small half-width  $(\Delta E \leq 25 \text{ meV})$  together with the sharp temperature dependence (see Fig. 9), allow to connect the peaks  $E_{1s}$  and  $E_{2s}$  with the first two terms of the hydrogen-like series of the Wannier-Mott exciton. According to Ref. [23], the electron transition is direct and occurs on the border of Brillouin zone at point X, where the distance between points  $X_1$  and  $X_4$  is smallest [67, 68]. The assumption of the hydrogen-like nature



Figure 2. Mirror reflection spectrum of LiH crystal cleft in liquid helium. Angle of incidence  $45^{\circ}$ .

† Earlier results, obtained as a rule, from oxidized and hydrated surfaces, and the historical account of controversial interpretations can be found in Ref. [41], which also contains an extensive bibliography up to 1985.



Figure 3. Temperature dependence of the energy of the peak maximum of n = 2s state of exciton in reflection spectrum of LiH crystal.



**Figure 4.** Reflection spectra of LiH crystal measured at: *1* – 2 K; *2* – 71 K; *3* – 138 K; *4* – 220 K; *5* – 228 K.

of the energy spectrum of excitons (especially in the region of the parabolic exciton zone with energy  $E \le 40$  meV [69]) in LiH crystals seems natural because:

(1) the observed ratio of intensities of the first two peaks in the reflection spectra, in accordance with the theory of Ref. [70] for direct allowed transitions, is close to the law  $n^{-3}$ , where *n* is the principal quantum number (see also Ref. [32]);

(2) in terms of energy, the distance between these two peaks ( $\Delta_{12}$ ) is much less than the energy of the longitudinal optical (LO) phonon ( $\hbar\omega = 140 \text{ meV}$  [71]) (see, for example,

Ref. [46]); for LiH the ratio is  $\Delta_{12}/\hbar\omega_{LO} = 0.3$ ; note for the sake of comparison that for excitons in CdS, where the model of large-radius excitons works well (see, for example, Ref. [72]), this ratio is 0.74 [18];

(3) the arguments in favor of the applicability of the Wannier–Mott model to excitons in LiH are supported by the fact that a similar structure, consisting as a rule, of two lines, is observed in the reflection spectra of many semiconductor crystals [17, 18, 72, 73].

On the strength of the arguments developed above, and with due account for the energies of the long-wave peaks  $E_{1s}$ and  $E_{2s}$ , we get the following value of the exciton Rydberg for LiH:  $E_b = 4/3\Delta_{12} = 42$  meV (where  $\Delta_{12} = E_{2s} - E_{1s}$ , and  $\Delta E_{2s} = 11$  meV). Here  $\Delta E_{2s}$  is the binding energy of the first excited exciton state. The value of  $\Delta E_{2s}$  found from the hydrogen-like formula for the binding energy of exciton (see above) agrees well with the above estimates of the energy of thermal ionization of the n = 2s exciton state. Independent measurement of the exciton binding energy in these crystals was also performed by temperature-induced quenching of the luminescence of free excitons. Assuming that quenching is caused by ionization of the ground state of an exciton, the binding energy in LiH was found to be  $40 \pm 3$  meV [34, 49]. Note also that the binding energy of an exciton in LiH calculated in Ref. [67] for the model of contact interaction is  $E_{\rm b} = 30 \text{ meV}.$ 

The small energy gap between the levels n = 1 s and n = 2 s of exciton states points to the strong screening of the Coulomb potential which binds the electron and the hole. The strong screening of the Coulomb potential points directly to the relatively large radius of the exciton state, and as a consequence, to the slowness of relative motion of bound carriers [23]. According to Ref. [21], the Coulomb potential must include the total value of dielectric permittivity (see also Ref. [14]). The relatively strong scattering of excitons by the LO photons ought to have led to a considerable dropout of the level with n = 1s from the Rydberg series (see also Ref. [74]). In our case, however, this is not so, since the deviation of the level of the n = 1s exciton state from the hydrogen-type model does not exceed 0.1  $E_b$  [75]. The line maximum of the n = 3s state in this series ought to occur at 4.987 eV. The power of the oscillator of this state is too low to be observed in the reflection spectra (cf. Ref. [76]).

Knowing the value of the binding energy of the exciton, we can find the energies of interband transitions:  $E_g = E_{1s} + E_b = 4.950 + 0.042 = 4.952$  eV (T = 2-4.2 K). For comparison, the value of this quantity according to band calculations varies (direct transition  $X_1-X_4$ ) from  $E_g = 6.61$  eV [67] to 5.24 eV [68], which points to a certain disagreement between theory and experiment.

#### 3. Band structure of LiH

It is impossible to comprehend the optical properties of solids without a detailed knowledge of their electron energy structure. The advent of fast and powerful computers in the 1960s stimulated a huge number of calculations of the band structures of various substances, including ionic crystals. Many different methods of calculation have been developed. A critical analysis of the results of calculations for broad-gap ionic crystals using the example of  $A_1B_7$  was performed in Ref. [77], together with a consistent comparison between theoretical calculations and experimental data. This comparison threw light on a number of conceptual problems which indicate that the calculation of the band structure of ionic crystals is not just a 'technical feat'. Moreover, some recognized experts (see, for example, Ref. [78]) tend to conclude that the very concept of band structure does not apply to ionic crystals.

The spectrum of one-electron states of a crystal is determined by the solution of Schrödinger equation for the 'extra' particle (hole or electron) moving in the averaged field created by all the remaining electrons and nuclei:

$$\left[-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r})\right]\psi_{\mathbf{K}}(\mathbf{r}) = E_n(\mathbf{K})\psi_{\mathbf{K}}(\mathbf{r}), \qquad (3)$$

where the notation is conventional, and  $V(\mathbf{r})$  is the periodic potential. The existing calculation techniques differ in the method of constructing the electron potential  $V(\mathbf{r})$ , the approximation of the wave function  $\psi_{\mathbf{K}}(\mathbf{r})$ , the ways of ensuring self-consistency, and the reliance on empirical parameters, etc. In particular, two factors are especially important in the case of ionic crystals: (1) the inclusion of the exchange interaction, and (2) the inclusion of the polarization of the electron and ion subsystems of the crystal by the extra particle [79].

The one-electron potential of any many-electron system is non-local because of the exchange interaction between the electrons. It is very difficult to take this interaction into account. Because of this, the exact potential in the band theory is often replaced by a local potential of the form  $V_{\text{exc}}(\mathbf{r}) \propto \alpha [\rho(\mathbf{r})]^{1/3}$ , where  $\rho(\mathbf{r})$  is the charge density function, and the constant  $\alpha$  is selected in the range 1 (the Slater potential) to 2/3 (the Cohn–Sham potential) [80].

Two effects are associated with the local exchange. Firstly, the results of the calculation depend strongly on the numerical value of  $\alpha$ , and secondly, this approximation always underestimates the values of  $E_{\rm g}$  and  $E_{\rm v}$  (the width of the valence band). It is the low values of  $E_v$  obtained by many authors in the approximation of local exchange that are responsible for the wrong conclusion concerning the inapplicability of band theory to ionic dielectrics. These problems reflect the fundamental drawback of the one-electron approximation which does not take into account the reciprocal effect of the selected electron (hole) on the rest of the system. This effect consists in the polarization of the crystal by the particle, and is generally made up of two parts: the electron polarization (inertialess), and the lattice polarization (inertial). In common optical phenomena, related to absorption or scattering of photons, the lattice polarization is not important, because the frequency of optical transitions is much higher than the average frequencies of phonons. The electron polarization is different. The extra particle (electron or hole) is regarded by this theory as the slowest particle in the system in other words, all the remaining electrons follow it adiabatically. Hence it follows that the inertialess polarization must definitely be included in the calculation of the energy spectrum. An important feature of ionic crystals is that the polarization energy  $E_p$  is of the same order of magnitude as the bandwidth. Such a correction obviously cannot be regarded as small. In the extreme case of a particle at rest, the polarization energy can be calculated by methods of classical electrostatics (the Mott-Littleton method [79]), or by the newer and more accurate technique proposed by Fowler [81]. The value of  $E_p$  for AHC found by this method is 2–3 eV for each of the quasi-particles ( $E_p > 0$  for electrons, and  $E_p < 0$ for holes). This implies that the inclusion of the electron polarization will reduce the magnitude of  $E_g$  by 4–5 eV [77]. By assumption, the electron bands are displaced rigidly, without changing the dispersion law  $E(\mathbf{K})$ .

The simple electron structure of lithium hydride (combined with the negligibly small spin-orbit interaction) is very helpful for calculating the band structure: all electron shells can easily be taken into account in the construction of the electron potential.

The first calculations of band structure of lithium hydride were carried out as early as in 1936 by Ewing and Seitz [82] using the Wigner–Seitz cell method. This method consists essentially in the following. The straight lattice is divided into polyhedra in such a way that the latter fill the entire space; inside each polyhedron is an atom forming the basis of the lattice (Wigner–Seitz cells). The potential inside each cell is assumed to be spherically symmetrical and coincide with the potential of a free ion. This approximation works well for ions with closed shells. The radial Schrödinger equation in the coordinate function  $R_l(\mathbf{r})$  is solved within each selected cell, the energy being regarded as a parameter. Then the Bloch function is constructed in the form of the expansion

$$\psi_{\mathbf{K}}(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} C_{lm}(\mathbf{K}) Y_{lm}(\boldsymbol{\Theta}, \boldsymbol{\varphi}) R_{l}(\mathbf{r}, E), \qquad (4)$$

where  $r, \Theta, \varphi$  are the spherical coordinates (with respect to the center of the cell);  $Y_{lm}$  are spherical functions. The coefficients  $C_{lm}(\mathbf{K})$  and the energy  $E(\mathbf{K})$  are found from conditions of periodicity and continuity on the boundaries of the cell. If  $\mathbf{r}_1$  and  $\mathbf{r}_2$  are the coordinates of two points on the surface of Wigner–Seitz cell, linked by the translation vector  $R_l$ , then the boundary conditions are [82]

$$\begin{split} \Psi_{\mathbf{K}}(\mathbf{r}_{2}) &= \exp(i\mathbf{k}\mathbf{R}_{l})\Psi_{\mathbf{K}}(\mathbf{r}_{1})\,, \end{split} \tag{5} \\ \nabla_{\mathbf{n}}\Psi_{\mathbf{K}}(\mathbf{r}_{2}) &= \exp(-i\mathbf{k}\mathbf{R}_{l})\nabla_{\mathbf{n}}\Psi_{\mathbf{K}}(\mathbf{r}_{1})\,, \end{split}$$

where  $\nabla_n$  is the gradient normal to the surface of the cell. We see that the method of cells only differs from the problem of the free atom in the boundary conditions. Owing to the complex shape of the cell, however, the construction of the boundary conditions is a very complicated task, and this method is rarely used nowadays.

The method of plane associated waves (PAW) was used for calculating the band structure and the equation of state for LiH was used in Ref. [83].

According to this method, the crystal potential is assumed to be spherically symmetrical within a sphere of radius  $r_S$ described around each atom, and constant between the spheres (the so-called cellular muffin-tin potential). Inside each sphere, as in the Wigner – Seitz method, the solutions of Schrödinger equation have the form of spherical harmonics; outside the spheres they become plane waves. Accordingly, the basis functions have the form

$$\Psi_{\mathbf{K}}(\mathbf{r}) = \exp(i\mathbf{k}\mathbf{r})\Theta(\mathbf{r} - \mathbf{r}_{s}) + \sum a_{lm}Y_{lm}(\Theta, \varphi) R_{l}(E, \mathbf{r})\Theta(\mathbf{r}_{s} - \mathbf{r}), \qquad (6)$$

where  $\Theta(x) = 1$  at  $x \ge 0$ , and  $\Theta(x) = 0$  at x < 0. The coefficients  $a_{lm}$  can easily be found from condition of sewing on the boundary of the sphere. This is an important advantage of the PAW method over the method of cells. The calculations of Ref. [83] are self-consistent, and the local potential is used in the Cohn–Sham form. The correlation corrections were neglected.

The method of Corringi-Cohn-Rostocker (the CCR method), or the method of Green's functions, was used for calculating the band structure of LiH in Ref. [84] (only concerned with the valence band) and Ref. [85]. Calculation of the band structure of LiH in Ref. [86] was based on the wave function used in the method of orthogonalized plane waves of the form

$$\Psi_{\mathbf{K}}(\mathbf{r}) = \exp(i\mathbf{kr}) - \sum \langle \exp(i\mathbf{kr}) | X_{c} \rangle X_{c}(\mathbf{r}) ,$$

where  $X_c$  are the atomic functions of state of the skeleton;  $\langle \exp(i\mathbf{kr})|X_{c}\rangle$  is the integral of the overlapping of the plane wave with a skeleton function (see also Ref. [68]). The method of linear combination of local basis functions was applied to the calculation of the band structure of LiH in Ref. [67]. This method is based on constructing local orbitals for the occupied atom states, based on certain invariant properties of the Fock operator. The main feature of local orbitals is that they are much less extensive than the atom orbitals. Importantly, the correlation correction is taken into account in Ref. [67]. Owing to the high polarizability of hydrogen molecules, the correlation effect in lithium hydride is exceptionally strong. Yet another calculation of the band structure of LiH was carried out in Ref. [84] using the socalled method of extended elementary cells [87]. This approach is based on the semi-empirical techniques of the theory of molecules, and is largely similar to the cluster calculations. Let us add that the cluster is selected in such a way that the quasi-molecular wave function transforms in accordance with the group symmetry of certain wave vectors in the Brillouin zone. This methods only yields energy values at the points of high symmetry. We ought also to mention Ref. [88] where, in connection with the study of high pressure effects on the transition NaCl-CsCl in lithium hydride, the band structure and the equation of state of the latter are analyzed in detail.

The calculated band structures of LiH are compared in Fig. 5. We see that the overall picture given by various methods is generally the same, despite the vast spread of the transition energy values (see Table 2). Looking at the

**Table 2.** Calculated energy values of some direct optical transitions in LiH reduced to the experimental value of  $E_g = 5.0$  eV.

<b></b>	Source				
Iransition	[67]	[83]	[86, 68]	[85]	
$K_1 - K_3$	6.9	7.5	6.5	6.4	
$W_1 - W_3$	8.0	7.9	7.3	7.4	
$L_1 - L'_2$	9.2	9.6	9.0	9.1	
$W_1 - W_2'$	12.6	14.9	12.2		
$X_1 - X_5'$	12.9	13.8	13.6		
$K_1 - K_4$	14.7	16.1	15.0		
$L_1 - L'_3$	19.7	20.9	20.7		
$\Gamma_1 - \Gamma_{15}$	24.5	25.3	33.3		

structure of the valence band we see that it is very similar to the S-band in the method of strong bonds (see also Ref. [77]). This is surprising, given the strong overlap of the anion Sfunctions in lithium hydride. The wave functions in this band are almost entirely composed of the 1s-states of the hydrogen ion. Different authors place the ceiling of the band either at point X or at point W of the Brillouin zone. Although in all cases the energies of the states  $X_1$  and  $W_1$  differ little ( $\leq 0.3$  eV), the question of the actual location of the top of the valence band may be important for the dynamics of the hole. Different calculations also disagree on the width of the valence band. For example, the width of the valence band in LiH without correlation, according to Ref. [67], is  $E_{\rm v} = 14.5$  eV, and the value of  $E_{\rm v}$  is reduced to one half of this when the correlation is taken into account. This shows how much the polarization of the crystal by the hole affects the width of the valence band  $E_{\rm v}$ . According to Ref. [83], the width of the valence band in LiH is 5.6 eV. The density of electron states in the valence band of LiH was measured in Refs [89, 90]. In Ref. [89] the measurements were carried out with a magnetic spectrometer having a resolution of 1.5 eV, whereas the resolution of hemispherical analyzer used in Ref. [90] was 1.1 eV. From experimental data, the width of the valence band is 6 eV according to Ref. [89], and 6.3 eV according to Ref. [90]. Observe the good agreement with the



Figure 5. Band structure of LiH crystal as calculated in Ref. [67] (a); Ref. [83] (b); Ref. [68] (c).

calculated value of  $E_v$  in this theory. Let us also add that the measured distribution of the electron density of states in the valence band of LiH exhibits an asymmetry typical of S-bands (for more details see Refs [89, 90]).

The lower part of the conduction band is formed wholly by p-states and displays an absolute minimum at point X which corresponds to the singlet symmetry state X<sub>4</sub>. The inversion of order of s- and p-states in the spirit of the LCAO method may be understood as the result of the s-nature of valence band [84]. The mixing of s-states of the two bands leads to their hybridization and spreading, which changes the sequence of levels. If we compare the structure of the conduction band with the p-band of the method of strong bonds [91], we see that the general structure and sequence of levels are the same except for some minor details (the location of the L<sub>3</sub> level, and the behavior of  $E(\mathbf{K})$  in the neighborhood of  $\Gamma_{15}$ ). In other words, the lower part of the conduction band in lithium hydride is very close to the valence p-band of AHC. The direct optical gap in LiH, according to all calculations, is located at the X point and corresponds to the allowed transition  $X_1 - X_4$ . The indirect transition  $X_1 - X_4$  ought to have a similar energy. According to the above calculations, the energies of these transitions differ by 0.03-0.3 eV. The different values of  $E_{\rm g}$  for LiH obtained by different authors are apparently due to the various methods used for taking into account the exchange and correlation corrections (see above). As follows from Table 2, the transitions at critical points in the low-energy region form two groups at 7-9 and 13-15 eV. Measurements of reflection spectra in the 4-25 eVrange at 5 K [50] and 4-40 eV at 300 K [42] throw new light on the results of calculations. The singularities occurring at 7.9 and 12.7 eV in the reflection spectra are associated in the above papers with the interband transitions  $W_1-W_4$  and  $X_1 - X_5$  respectively.

From the standpoint of the dynamics of quasi-particles, an important consequence of this band structure is the high anisotropy of the tensor of effective mass of electrons and (especially) holes. The estimated mass of an electron in the neighborhood of X<sub>4</sub>, according to Ref. [67], is  $(m_{\rm e})_{\rm x} \approx 0.3 \, m_0$  in the direction  $\rm X - \Gamma$ , and  $(m_{\rm e})_{\rm y} =$  $(m_{\rm e})_{\rm z} \approx 0.8 \, m_0$  in the direction X–W. Similarly, the mass of a hole in the neighborhood of  $X_1$  is  $X - \Gamma$  in the direction  $(m_{\rm e})_{\rm r} \approx 0.55 \, m_0$ , and about the same in the neighborhood of  $W_1$ . It is assumed that the transverse components of  $m_h$  are greater by several orders of magnitude [84]. Also note that, according to Ref. [68], the estimated masses of the carriers are:  $m_{\rm el} = 0.121$ ;  $m_{\rm et} = 0.938$ ;  $m_{\rm hl} = 0.150$ ;  $m_{\rm ht} = 4.304 m_{\rm e}$ , where the subscripts I and t denote, respectively, the longitudinal (in the direction  $\Gamma$ -X) and the transverse (in the direction X-W components. This high anisotropy of masses of electrons and holes ought to have resulted in the high anisotropy of the reduced  $(1/\mu = 1/m_e + 1/m_h)$  and translation  $(M = m_e + m_h)$  masses of the exciton. This, however, is not the case. Moreover, the study of Ref. [69] reveals that with a good degree of confidence one may assume that in the energy range  $E \leq 40$  the exciton band is isotropic and exhibits parabolic dispersion. As will be shown below, studies of exciton-phonon luminescence of free excitons and RRLS in LiH crystals [56, 57] reveal that the kinetic energy of excitons in these crystals is greater than  $E_{\rm b}$  by an order of magnitude exactly because of the very small masses of exciton and hole.

Let us now dwell a while on the problem of the dielectric – metal transition in LiH under external pressure. As the lattice

constant decreases, the forbidden gap in dielectrics narrows and eventually vanishes — the transition from dielectric to metal takes place. For typical dielectrics, the critical pressure exceeds several Mbar. The interest in the 'metallization' of lithium hydride is primarily due to the fact that its properties in the metallic phase may to a certain extent simulate the properties of metallic hydrogen. Indeed, owing to the presence of the broad hydrogen s-band and the strong expulsion of the s-band of Li in LiH, the Fermi level in the metallic phase ought to fall into the band created primarily by the electrons of hydrogen. Because of the high frequencies of optical oscillations, one could expect that metallic lithium hydride ought to go over into a superconducting state at a high enough temperature [1]. The usefulness of hydrides of alkaline metals at superhigh pressures as systems simulating metallic hydrogen is discussed in detail in the review [93].

Intuitively, the idea of metallization of lithium hydride at relatively low pressures seems quite plausible. As a matter of fact, the outer electron of  $H^-$  is rather strongly delocalized even at normal pressure. Since the overlap of wave functions increases exponentially as the lattice constant decreases, one may expect that a moderate amount of compression will result in complete delocalization of this electron.

The pressure of the dielectric-metal transition in LiH was calculated in Refs [83, 85, 88, 94-96]. Such a calculation is usually carried out in two steps: first, the width of the forbidden gap (or the entire band structure) is calculated as a function of the lattice parameter, and then in some way or other the equation of state which links the lattice constant and the pressure is expressed. Strictly speaking, these two problems ought to be solved concurrently; so far, however, this has been only done in Refs. [82, 88], and then only for the electron contribution to the pressure.

The early calculations [94, 95] gave discouragingly high values of the critical pressure, from 23 to 25 Mbar, and accordingly, very small values of *a* in the metallic phase, from 1.3 to 2.2 A. Later, however, these results were found to be wrong because of a number of unreasonable assumptions. In Ref. [94], for example, it was assumed that the gap in LiH is indirect and corresponds to the  $W_1 - L_2$  interval (see Fig. 5). Then, the overlap of electron distributions in LiH was neglected, although the calculated value of the lattice constant (1.3 A) implies that the distance between lithium ions is much less than the sum of their ionic radii. A more detailed criticism of these studies can be found in Refs [83, 85, 88, 96].

Of much greater interest are the results obtained thereafter. In Ref. [93] it was demonstrated that at a=2.9 A, which corresponds to a pressure of 2 Mbar, the gap  $X_1-X_4$  closes. The bands, however, just come into contact with each other without overlapping, the latter being forbidden at point X from considerations of symmetry. Accordingly, the Fermi surface is a point, and the system corresponds to a semimetal. As the lattice constant decreases further, the structure of the bands changes dramatically; in particular, the minimum of the valence band goes over from point  $\Gamma$  to point L. At a = 1.96 A the bands overlap, and the system becomes a metal. The critical pressure turns out to be 30 Mbar.

The results of Ref. [85] are similar to those obtained in Ref. [83]; attention is drawn, however, to the following interesting circumstance. If one calculates the band spectrum under certain assumptions concerning the hypothetical structure of the CsCl-type structure, the gap (indirect) of lithium hydride in CsCl structure turns out to be close to zero.

The critical pressure for this structure is estimated at 0.5 to 1 Mbar. In other words, the structural phase transition NaCl-CsCl occurs before the gap in the NaCl structure is closed, and is accompanied by metallization of the crystal. This very interesting conclusion was further developed in Ref. [88]. In this study, a method similar to that employed in Ref. [83] was used for expressing the equation of state for lithium hydride in a shock wave. According to Ref. [88], the bands also overlap at point X with a subsequent lowering of point  $X_1$  (the bottom of p-type conduction band) with respect to point  $X_4$  (the top of the s-valence band) The overlap starts at P = 2.26 Mbar, which is 13% higher than reported in Ref. [83]. The relatively low pressure of the dielectric – metal transition in LiH ( $\sim 0.5$ Mbar) is also predicted in Ref. [96], whereas according to Ref. [97] the critical pressure is not less than 4 Mbar (see also Ref. [98]). The calculation of Ref. [88] indicates that the structural phase transition B1-B2 (NaCl-CsCl) ought to occur at the pressure 1.3-1.4 Mbar and temperature 200 K. A recent study [98] was concerned with the behavior of  $E_{\rm g}$  and the refractive index of CsH crystal ( $E_g = 4.4 \text{ eV}$  at P = 0 Mbar) as functions of the external pressure. No structural phase transition in CsH crystal could be observed over the broad range from 0 to 2.51 Mbar. According to the estimates made in this paper, the conduction and valence bands may start to overlap at about 10 Mbar. We see that studies of these aspects of lithium hydride are quite far from conclusion.

#### 4. Exciton – phonon interaction

4.1 Polarization interaction of free excitons with phonons The foundations of the theory of the exciton – phonon interaction were laid in the 1950s. Apart from the pioneering study [99], the interaction of excitons with the LO phonons was considered by many authors (see Refs [14, 21, 100-102]). In ionic crystals there are two main mechanisms of interaction of excitons with lattice vibrations. One mechanism - the short-range deformation interaction — is caused by the modulation of the wave function of the exciton by longitudinal acoustic vibrations. The magnitude of this interaction is characterized by the deformation potential (see below). The deformation interaction strongly affects the energy spectrum and the dynamics of excitons of relatively small radius (for example, the ground state of excitons in AHC and crystals of inert gases [14]). As the radius of an exciton increases, this interaction becomes less important, since the wave vector of actual phonons is  $q \propto r_{ex}^{-1}$  [103] (where  $r_{ex}$  is the exciton radius), and the number of such phonons is proportional to  $q^3$ .

The second mechanism — the polarization or Frohlich [104] interaction — is caused by the Coulomb interaction of the charge carriers forming the exciton with the macroscopic field created by the LO oscillations (see, for example, Ref. [101]). If the exciton radius is much greater than the lattice constant, then the exciton – phonon interaction may be regarded as the sum of independent interactions of the electron and hole with phonons (see Ref. [105]). The operator of interaction of charge of mass m ( $m_e$  or  $m_h$ ) with long-itudinal oscillations neglecting the dispersion of the latter is [104]:

$$H_{\rm el} = \sum_{q} W_{\rm q} \exp(\mathrm{i}\mathbf{q}\mathbf{r})(b_{-\mathbf{q}}^{+} + b_{\rm q}), \qquad (7)$$

where

$$W_q = -\frac{\hbar\omega_{\rm LO}}{|\mathbf{q}|} \left[\frac{4\pi q_{\rm e,h}^2}{V}\right]^{1/2},\tag{8}$$

V is the volume of the system, r are the coordinates of the particles. In these expressions we introduce the main parameters which determine the interaction of the electron (hole) with optical vibrations: the polaron 'radius'

$$r_{\rm e,\,h}^* = \left(\frac{\hbar}{2} \, m_{\rm e,\,h} \omega_{\rm LO}\right)^{1/2} \tag{9}$$

and the dimensionless Frohlich constant of interaction

$$g_{e,h}^2 = \frac{1}{\alpha} \left( \frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_0} \right) \frac{e^2}{\hbar \omega_{\rm LO} r_{e,h}^*} \,. \tag{10}$$

The first of these quantities characterizes the size of the region of polarization of the lattice by the extra charge, and the second describes the strength of the electron – phonon interaction (see also Refs [14, 21]).

As follows from Eqn (7), the operator of interaction  $W_{\mathbf{q}}$  does not depend on the mass of the quasi-particle, and is the same for electrons and holes. Accordingly, the Hamiltonian of interaction of Wannier–Mott excitons with optical phonons has the same form (7), the only difference being that  $\exp(i\mathbf{qr})$  is replaced with  $\exp(i\mathbf{qr}_e) - \exp(i\mathbf{qr}_h)$ , where  $r_{e,h}$  are the coordinates of the electron (hole). In the center-of-mass system, the operator of interaction becomes [99]

$$H_{\text{EXL}} = \sum_{q} W_{\mathbf{q}} \left[ \exp(i\mathbf{q}_{\mathbf{e}}\mathbf{r}) - \exp(i\mathbf{q}_{\mathbf{h}}\mathbf{r}) \right] (b_{-\mathbf{q}}^{+} + b_{\mathbf{q}}) .$$
(11)

Replacing  $m_{e,h}$  by the reduced mass  $\mu$  by analogy with Eqn (7), we can define the characteristic size of the polarization region  $r_{ex} = \left[\left(r_e^*\right)^2 + \left(r_h^*\right)^2\right]^{1/2}$  and the interaction constant  $g_{ex}^2$ . Making use of the characteristics of the Wannier–Mott exciton ( $r_{ex}$ ,  $E_b$ ), one can express the latter as

$$g_{\rm ex}^2 = \left(\frac{E_{\rm b}}{\hbar\omega_{\rm LO}}\right)^{1/2} \frac{\varepsilon_0}{\varepsilon_\infty} - 1 = \frac{r_{\rm ex}^*}{r_{\rm ex}} \left(\frac{\varepsilon_0}{\varepsilon_\infty} - 1\right),\tag{12}$$

where  $r_{\text{ex}} = a_0(\varepsilon_{m0}/\mu)$ , and  $a_0 = h^2/m_0e^2 = 0.53 \text{ A}$  is the Bohr radius of a hydrogen atom.

The scattering of excitons by the LO phonons is determined by the magnitude and the wave-vector dependence of the matrix element

$$H_{\text{EXL}}^{\lambda_1 \lambda_2} = \langle \psi_{\lambda_1} | H_{\text{EXL}} | \psi_{\lambda_2} \rangle , \qquad (13)$$

where  $\psi_{\lambda_1}$  and  $\psi_{\lambda_2}$  are the wave functions of the initial and final states of the exciton with the wave vectors  $k_1$  and  $k_2 = k_1 + q$ . The properties of the matrix element of exciton – phonon scattering, as first noted in Ref. [106], depend crucially on the parities of the initial  $\lambda_1$  and final  $\lambda_2$  states. If the parity is the same (scattering occurs within one and the same band, like 1s-1s or 2s-2s, etc., or in case of interband scattering 1s-2s, 1s-3s, etc.), this mechanism of exciton – phonon scattering is forbidden, because  $H_{\text{EXL}}^{\lambda_1 \lambda_2} \rightarrow 0$  at  $q \rightarrow 0$ . When excitons are scattered in a band of the ground state (1s-1s), as shown in Ref. [99], the matrix element has the form

$$H_{\text{EXL}}^{\lambda_1 \lambda_2} \propto \left(\frac{g_{\text{ex}}\omega_{\text{LO}}}{r_{\text{ex}}} |q|\right) \left\{ \left[1 + \left(\frac{q_{\text{e}}r_{\text{ex}}}{2}\right)^2\right]^{-2} - \left[1 + \left(\frac{q_{\text{h}}r_{\text{ex}}}{2}\right)^2\right]^{-2} \right\}.$$
(14)

When q is small (and it is the small values that are of special importance; see below), the matrix element is proportional to

$$H_{\mathrm{EXL}}^{\lambda_1 \lambda_2} \propto \left( \frac{m_{\mathrm{h}} - m_{\mathrm{e}}}{m_{\mathrm{h}} + m_{\mathrm{e}}} \right) q r_{\mathrm{ex}} \,.$$
 (15)

As follows from Eqn (15), the Frohlich mechanism of intraband scattering is absolutely forbidden when the effective masses are equal. This is because the centers of distribution of masses and charges coincide at  $m_e = m_h$ , and so the polarization interactions of electrons and holes cancel out completely.

In the general case, the matrix element (14) arrives at maximum near  $qr_{ex} \sim 1$ , and then falls off rapidly (Fig. 6). A similar behavior is displayed by the matrix elements of the scattering process between the states of the same symmetry (is-js, ip-jp, etc.). In such cases, the matrix element attains its maximum at the value of inverse radius  $(r_n)$  of the corresponding exciton state, that is,

$$q_{\max} \sim \frac{1}{nr} , \quad r_n = nr_1 . \tag{16}$$

According to Ref. [106], when scattering occurs between bands of different symmetry (*i*s-*k*p), the matrix element at q-0 tends to a constant (nonzero) value, and such a process is therefore allowed. As in our first case, however, the matrix element  $H_{\text{EXL}}^{\lambda_1\lambda_2}$  falls off rapidly as  $q > r_{\text{ex}}^{-1}$  increases. The dependence of matrix elements on q for some cases of allowed and forbidden scattering for CdS is discussed in Ref. [102].

The behavior of matrix elements (14) is definitive for the structure and properties of luminescence spectra of free excitons and Raman scattering in the resonance region. The existing theory of exciton – phonon interaction describes the case of an isotropic band with a parabolic dispersion of exciton states. Its successful application to LiH (with the high anisotropy of the valence band, see Fig. 5) once again testifies to the fact that the dispersion of the exciton band is indeed parabolic [69] in the range of low exciton kinetic energies. Let us also add that, according to Ref. [102], the



**Figure 6.** Dependence of the matrix element of intraband scattering on  $qr_{ex}$  for the mass ratio  $m_h/m_c = 3.5$  [107].

exciton band exhibits a parabolic dispersion even for such an anisotropic crystal as CdS, which is supported by the successful application of the theory of exciton – phonon interaction to the analysis of spectra of luminescence and RRLS of free excitons in CdS crystals.

#### 4.2 Effects of temperature and pressure on exciton states

Even after the first works on the spectroscopy of large-radius excitons (see Ref. [16]) it became clear that the location of the edge of fundamental absorption (and hence the exciton structure) in a solid depends on the temperature. Further studies also revealed (see also Refs [14, 19]) that the temperature dependence of the absorption edge may be caused by two factors: by expansion of the lattice, and by lattice vibrations. Vibrations of the lattice will cause not only displacement but also broadening of the energy levels of electron excitations. As was first shown in Ref. [108], the change in the energy of band-to-band transitions  $\Delta E_g$  in most substances is caused primarily by the displacement of the energy levels rather than by their broadening as had been assumed before.

In Ref. [108] it was demonstrated that in the mechanism of the deformation potential of the electron – phonon interaction the quantity  $\Delta E_{g}$  is directly proportional not only to the square of the deformation potentials of the valence band and the conduction band, but also to the sum of  $q_{\text{max}}$  and  $q_{\text{max}}^2$ , where  $q_{\text{max}}$  is the maximum value of the wave vector of the phonon. If the displacement of electron bands (or exciton levels) associated with the Frohlich mechanism of the electron - phonon interaction is taken into account, the matrix element is inversely proportional to the wave vector of phonons (see Refs [8, 13]). There is an important distinction between displacement and broadening of energy levels. The point is that in the case of displacement the theory considers virtual transitions, whereas in the case of broadening the transitions are real. Real transitions require conservation of quasi-momentum and energy, whereas only quasi-momentum must be conserved in the case of virtual transitions. In the mechanism of the deformation potential this circumstance is especially important for acoustic vibrations, being associated with the directly proportional dependence of the matrix element of the electron transition in the magnitude of the wave vector of the phonon. And since virtual transitions may involve phonons with not necessarily small values of q, it becomes clear why in the mechanism of the deformation potential of the electron - phonon interaction the displacement of energy levels much exceeds their broadening (for more details see Ref. [109]).

The contemporary microscopic treatment of this problem (see, for example, Ref. [110]) singles out four contributions to the temperature dependence of  $E_g$  (see also Ref. [58]):

(1) the Debye–Waller factor in the Fourier expansion of the periodical part of the crystal potential;

(2) the term related to intraband transitions, now commonly referred to as the Fan term [111];

(3) the contribution from band-to-band transitions, which is currently hard to evaluate;

(4) the contribution from thermal expansion of the crystal lattice.

As a rule, the majority of experimental studies concerned with this problem (see, for example, Ref. [111] and references therein) consider two contributions: the contribution from the electron – phonon interaction, expressed as either the Debye–Waller or the Fan term, and the contribution from thermal expansion of the lattice. A consistent study of the effects of temperature on the energy of band-to-band transitions for a large number of semiconductor compounds [112-114] indicates that theory can be brought into good agreement with experiment when at least the first three factors are taken into account. Incidentally, it ought to be noted that, apart from the microscopic approach to the temperature dependence  $E_g(T)$ , attempts to explain the empirical formula of this dependence have continued for over three decades. First of all we should mention the well-known Varshni formula [115], widely used in experimental works, and the currently no less popular Manoogian–Leclea relation (see Refs [116, 117] and references therein).

The similar long-wave structure of spectra of mirror reflection of pure (LiH, LiD) and isotopically mixed crystals (see below; Fig. 8) allow its attribution to the excitation of the first and second exciton states [24]. As the temperature increases, the exciton reflection spectra of pure (see Fig. 4) and mixed crystals shift towards the longer waves as a whole. The exciton structure of reflection spectra broadens. In the temperature range from 2 to 200 K the line of the exciton ground state broadens approximately five-fold. At  $T \ge 130$ -140 K the peak caused by the exciton excitation in the state n = 2s becomes indiscernible in the spectrum (Fig. 4). The reflection spectra of  $LiH_xD_{1-x}$  crystals, including LiD, behave in a similar way. Figure 7 shows the temperature dependence of the energy of the long-wave maximum in the reflection spectrum for three crystals. For all three crystals, the dependence  $E_{n=1s} \sim f(T)$  in the temperature range  $T \ge 140$  K is well approximated by a linear function. The resulting temperature coefficients of linear shift are given in Table 3. We see that the temperature coefficient dE/dT is larger for the heavier isotope. Assuming that the temperature



**Figure 7.** Calculated temperature drift of the location of maximum of the 1s exciton state in the reflection spectrum of crystals: I - LiH;  $2 - \text{LiH}_{0.25}D_{0.75}$ ; 3 - LiD. Experimental values shown by points.

**Table 3.** Values of parameters calculated by formula (20), and values of temperature coefficients of line shift.

Crystals	$E_m(0), \mathrm{meV}$	A, meV	$\hbar\omega_{\rm eff},{\rm meV}$	$dE_{n=1s}/dT$ , meV K <sup>-1</sup>
LiH	4961	$12 \pm 1$	$11 \pm 1$	$\begin{array}{c} 0.19 \pm 0.01 \\ 0.22 \pm 0.01 \\ 0.28 \pm 0.01 \end{array}$
LiH <sub>0.25</sub> D <sub>0.75</sub>	5018	$15 \pm 1$	$12 \pm 1$	
LiD	5016	$17 \pm 1$	$13 \pm 1$	

shift is caused by the interaction of excitons with optical vibrations, we have

$$\frac{\mathrm{d}E_1}{\mathrm{d}T} = \frac{4}{3} \frac{\mathrm{d}E_2}{\mathrm{d}T} + \frac{E_1(0) - E_2(0)}{\langle T \rangle} , \qquad (17)$$

where  $dE_1/dT = dE_{n=1s}(\text{LiD})/dT$ ;  $dE_2/dT = dE_{n=1s} \times (\text{LiH})/dT$ ;  $T = \hbar\omega_{\text{LO}}(\text{LiD})/k$  and  $E_1(0)$ ,  $E_2(0)$  are the values of the maximum of the exciton band of LiD and LiH respectively at T = 0 K. Substituting the values of the quantities involved ( $\hbar\omega_{\text{LO}} = 104 \text{ meV}$  [118]) we find that the magnitude of  $dE_{n=1s}/dT$  for LiD is 0.34 meV K<sup>-1</sup>. Comparing this with the experimental value (0.28 meV K<sup>-1</sup>) we see that there is a rather large discrepancy, which will be discussed a little later.

In accordance with the arguments developed above, the temperature dependence of  $E_{n=1s}$  (as well as that of  $E_g$ ) is shaped by two contributions: the lattice expansion, and the exciton - (electron) - phonon interaction which is a sum of three terms. The first of the above can be found by evaluating the baric shift of  $E_{n=1s}$ . It is well known that the effects of pressure on the spectra of fundamental absorption is generally associated with changes in the width of the forbidden band, in the probabilities of transitions, and in the effective masses of carriers (see, for example, Ref. [119]). For non-degenerate states, it is usually only the change in  $E_{\rm g}$ that is of practical importance. Then one may expect that the exciton series shifts as a whole, without any significant changes in the binding energy and the intensities of individual lines (see also Ref. [16]). When the pressure P is relatively small (when the pressure-induced change in the energy of a given state is much less than the distance to the adjacent levels), the band shift may be assumed to be a linear function of the pressure. In this approximation the pressure dependence of  $E_g$  (and hence  $E_{n=1s}$ ) may be expressed as

$$E_{\rm g}(P) = E_{\rm g}(0) - (E_1^{\rm c} - E_1^{\rm v}) k_T P, \qquad (18)$$

where

$$k_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T; \quad E_1 = V \frac{\partial E}{\partial V}.$$
 (19)

In Eqns (18), (19)  $k_T$  is the isothermal compressibility and the hydrostatic deformation potential ( $E_d$ ); the superscripts c and v stand for the conduction band and the valence band. The deformation potential  $E_d$  in LiH we estimate from the results of Ref. [97]. This study was concerned with measuring the energy of the maximum of long-wave peak of mirror reflection of LiH crystal as a function of external hydrostatic pressure ( $P \le 330$  kbar). The absence of exciton structure (except for the n = 1s state) in the reflection spectrum (see also Fig. 4) at room temperature leads to the assumption that the binding energy of the exciton does not depend on the pressure, and therefore the function  $E_{n=1s} = f(P)$  uniquely defines  $E_g \sim f(P)$ , and vice versa. In Ref. [97] it was shown that in the pressure range  $40 \leq P \leq 330$  kbar this shift is linear with the baric coefficient  $\dagger \partial E / \partial P = -1.1$  meV kbar<sup>-1</sup>. According to Ref. [121],  $k_T \approx 3 \times 10^{-6}$  bar<sup>-1</sup>. Then  $E_d = 0.36$  eV for LiH. Apart from this low value of  $E_d$ , one should also note the non-monotonic dependence  $E_{n=1s} = f(P)$ : at  $P \leq 40$  kbar, according to the calculations of band structure in Refs [83, 85], the quantity  $E_{n=1s}$  (and hence  $E_g$ ) increases, and after  $P \geq 40$  kbar, decreases linearly. This behavior of the exciton (n = 1s) maximum in the reflection spectrum may be attributed to two factors:

(1) Removal of the ban with respect to **K** on the electron transition  $W_1-X_4$ , which is estimated theoretically to lie 0.03 eV below the direct  $X_1-X_4$  transition in LiH (for more details see Ref. [23]).

(2) Excitation, as the pressure increases, of the higher pstates in the conduction band, as noted earlier in Refs [55, 88].

These two factors may also work simultaneously, which on the other hand, may be responsible for the low value of  $E_d$ characteristic of electron transitions occurring at points other than  $\Gamma$ -point of the Brillouin zone (cf. Ref. [121]). Let us also add that for most semiconductor compounds with the structure of diamond (or zinc blende) the rate of change  $(\partial E_g/\partial P)$  of the quantity  $E_g$  at points  $\Gamma$ , X, and L, on the average, is 12, -1.5, and 5 meV kbar<sup>-1</sup>, respectively [122, 123], and thus differs not only in magnitude, but also in sign (for more details see Ref. [119]).

The obtained value of  $E_d$  allows one to estimate the contribution of the lattice expansion to the change in  $E_{n=1s}$ . It constitutes 12% at low temperatures, and 20% at room temperature of the entire shift for LiH crystals. We see that the main change in  $E_{n=1s}(E_g)$  comes from the Debye–Waller term and the term which accounts for the internal energy (the Fan term). As demonstrated in Refs [112–114], the inclusion of the latter two terms (which, incidentally, have opposite signs) along with the lattice expansion brings the theory into good agreement with the experimentally observed dependence  $E_g \sim f(T)$ .

The microscopic calculation of the temperature shift of  $E_g$  indicates [78] that this shift can only be related to those terms in the expansion of the potential energy which are quadratic with respect to displacement (see below, Refs [111–114]). In the one-oscillator Einstein model the dependence of  $E_g$  on T may be represented as

$$E(T) = E(0) - A \coth\left(\frac{\hbar\omega_{\rm eff}}{2k_{\rm B}T}\right),\tag{20}$$

where E(0) is the value of  $E_g(E_{n=1s})$  at T = 0, and  $\hbar \omega_{\text{eff}}$  is the effective frequency of the phonon in the model under consideration.

The temperature dependence of the maximum location of exciton peak in the reflection spectra of pure and mixed crystals, calculated according to Eqn (20), is shown in Fig. 7 by a solid line. As follows from Fig. 7, there is good enough agreement between the theoretical curves and experimental data. The calculated energy of the actual phonons  $\hbar\omega_{\rm eff}$ , as

†Observe also that, according to Ref. [98] the baric coefficient takes on two values:  $\partial E/\partial P = -4.6 \pm 2 \text{ keV } \text{kbar}^{-1}$  in the range  $0 \le P \le 300 \text{ kbar}$  and  $\partial E/\partial p = -0.237 \pm 0.001 \text{ meV } \text{kbar}^{-1}$  in the range  $300 \le P \le 2510 \text{ kbar}$ . It should be noted that, by contrast to LiH, the value of  $E_g$  in CsH starts to decrease immediately after the application of external pressure.

can be seen from Table 3, falls into the range of acoustic vibrations. The latter seems to point to the domination of the mechanism of the deformation potential of the electron – (exciton) – phonon interaction. This is a reasonable conclusion, if we recall that the energy of an LO phonon is 104 meV for LiD, and 140 meV for LiH [118]. This apparently also explains the discrepancy between the theoretical and experimental values of the linear temperature coefficient dE/dT (see above).

Linear extrapolation (harmonic approximation) of the location of the maximum of the long-wave exciton peak  $E_{n=1s}$  to T = 0 K yields E(0) = 4962 meV for LiH and 5066 meV for LiD. These results agree well with the calculated values (see the second column in Table 3). The difference between these two extrapolations is 104 meV, which practically coincides with the experimental value at T = 2 K;  $\Delta E_g = E_g(\text{LiD}) - E_g(\text{LiH}) = 103$  meV [124]. Assuming that this value is wholly determined by the interaction of electrons with zero oscillations of the lattice, we may evaluate it using the Fan approximation [109]:

$$\Delta E_{\rm g}(\exp) = \delta E_{\rm g}\left(\frac{M_1}{M_2} - 1\right),\tag{21}$$

where  $M_1$ , and  $M_2$  are the masses of light and heavy isotopes,  $\delta E_{\rm g}$  is the narrowing of the forbidden gap because of the above interaction,  $\Delta E_{g}(exp)$  is the experimentally observed narrowing of  $E_g$  equal to 103 meV. Obviously, in the case of LiH and LiD the masses  $M_1$  and  $M_2$  must be replaced with the reduced masses of the elementary cell:  $\mu_{\text{LiH}} = 7/8$  and  $\mu_{\rm LiD} = 14/9$ . Substituting these values into Eqn (21), we find that  $\delta E_{g} = 412$  meV. Then the 'actual' (the crystal lattice not perturbed by zero oscillations) width of the forbidden gap in LiH is  $E_g = 4992 + 412 = 5404$  meV, which is more than 300 meV (more than twice the energy  $\hbar\omega_{LO}$  for LiH) greater than  $E_g$  at 2 K for LiD (5095 meV, see Table 4). This mismatch between experiment and theory (harmonic approximation) is too large. Observe that for isotopic substitution in ZnO [125], Ge [126] and diamond [127] a similar theoretical evaluation of  $\delta E_g$  by Eqn (21) is in good agreement with experiment. At present the reason behind such a striking disagreement in case of LiH is not quite clear. There are, however, at least two features which fundamentally distinguish LiH from ZnO, Ge and C - namely, that isotopic substitution greatly changes the scattering potential [28], and zero oscillations give a substantial contribution to anharmonism. Indeed, the energy of zero oscillations in the Debye approximation for a two-atom crystal is [109]  $E_0 \approx (9/8 k_{\rm B} \Theta)$ , where  $\Theta$  is the Debye temperature. Given that  $\Theta = 1190 \pm 80$  K for LiH [130], we find that  $E_0 \approx 115$ meV, which is close to the energy of an LO phonon and much greater than  $E_{\rm b}$  — in other words, it is not at all small. To end this section, let us add that the different temperature

**Table 4.** Values of the energy of maxima in exciton reflection spectra of pure and mixed crystals at 2 K, and energies of exciton bond  $E_{\rm b}$  and band-to-band transitions  $E_{\rm g}$ .

Energy, meV	LiH	LiH <sub>0.82</sub> D <sub>0.18</sub>	LiH <sub>0.40</sub> D <sub>0.60</sub>	LiD	Li <sup>6</sup> H (78 K)
$E_1$	4950	4967	5003	5043	4939
$E_2$	4982	5001	5039	5082	4970
$E_{\rm b}$	42	45	48	52	41
$E_{\rm g}$	4992	5012	5051	5095	4980

dependence of exciton peaks of n = 1s and 2s states leads to the temperature dependence of the binding energies of Wannier-Mott excitons — this problem has not received any adequate treatment. More specifically, the energy  $E_b$  in LiH crystals [24] decreases with increasing temperature, whereas  $E_b$  increases for excitons of the green and yellow series in Cu<sub>2</sub>O crystals [131].

#### 4.3 Isotopic effect on electron excitations

4.3.1 Renormalization of the energy of band-to-band transitions in the case of isotopic substitution. Isotopic substitution only affects the wave function of phonons; therefore, the energy values of electron levels in the Schrödinger equation ought to have remained the same. This, however, is not so, since isotopic substitution modifies not only the phonon spectrum, but also the constant of electron - phonon interaction (see above). It is for this reason that the energy values of pure electron transitions in molecules of hydride and deuteride are found to be different [132]. This effect is even more prominent when we are dealing with a solid. This conclusion was confirmed on a qualitative level as early as the 1930s in Ref. [34]. Comparison of absorption spectra for thin films of LiH and LiD at room temperature revealed [34] that the long-wave maximum (as we know now, the exciton peak) moves 64.5 meV towards the shorter wavelengths when H is replaced with D. For obvious reasons this fundamental result could not then receive a consistent and comprehensive interpretation, which however does not belittle its importance even today. As will be shown below, this effect becomes even more pronounced at low temperatures.

The spectra of mirror reflection of mixed and pure LiD crystals cleft in liquid helium are presented in Fig. 8. For comparison, on the same diagram we have also plotted the reflection spectrum of clean surface LiH crystals. All the spectra were measured with the same apparatus under the same conditions. As the concentration of deuterium increases, the long-wave maximum broadens [133] and shifts towards the shorter wavelengths. As can be seen clearly in Fig. 8, all the spectra exhibit a similar long-wave structure. This circumstance allows one to attribute this structure to the excitation of the ground (1s) and the first excited (2s) exciton states. The energy values of exciton maxima for pure and mixed crystals at 2 K are presented in Table 4. The binding energies of excitons  $E_b$ , calculated using the hydrogen-like formula, and the energies of the interband transitions  $E_{g}$  are also given in Table 4. The ionization energy, found from the temperature quenching of the peak of the reflection spectrum of the 2s state in LiD is 12 meV. This value agrees fairly well with the value of  $\Delta E_{2s}$  calculated using the hydrogen-like formula. Moreover,  $E_{\rm b} = 52$  meV for LiD agrees well with the energy of activation for thermal quenching of the luminescence of free excitons in these crystals [3].

Going back to Fig. 8, it is hard to miss the growth of  $\Delta_{12s}$  [24, 133], which in the hydrogen-like model causes the increase of the exciton Rydberg with the replacement of isotopes (Fig. 9). When hydrogen is completely replaced with deuterium, the exciton Rydberg (in the Wannier–Mott model) increases by 20% from 40 to 50 meV, whereas  $E_g$  exhibits a 2% increase, and at 2–4.2 K is  $\Delta E_g = 103$  meV. This quantity depends on the temperature, and at room temperature is 73 meV [74], which agrees well enough with  $\Delta E_g = 64.5$  meV as found in Ref. [34]. The continuous change of the exciton Rydberg had earlier also been observed in the crystals of solid solutions A<sub>3</sub>B<sub>5</sub> [135, 138] and A<sub>2</sub>B<sub>6</sub> [139, 140].



**Figure 8.** Mirror reflection spectra of crystals: I - LiH;  $2 - \text{LiH}_x D_{1-x}$ ; 3 - LiD at 4.2 K; 4 - light source spectrum measured without crystal.Spectral resolution of instrument is indicated on the diagram.



Figure 9. Binding energy of Wannier – Mott excitons as a function of the reduced mass of ions. Based on values of the reduced mass of ions for Li<sup>6</sup>H, Li<sup>7</sup>H, Li<sup>6</sup>D, Li<sup>7</sup>D, and LiT.

Isotopic substitution of the light isotope ( $S^{32}$ ) by the heavy one ( $S^{34}$ ) in CdS crystals [141] reduces the exciton Rydberg, which was attributed to the tentative contribution from the adjacent electron bands (see also [142]), which however, are not present in LiH (for more details see Refs [67, 68]). The single-mode nature of exciton reflection spectra of mixed crystals LiH<sub>x</sub>D<sub>1-x</sub> agrees qualitatively with the results obtained from the virtual crystal model (see, for example, Refs. [28, 143]), being at the same time its extreme realization, since the difference of ionization potentials ( $\xi$ ) for this compound is zero. According to the virtual crystal model,  $\xi = 0$  implies that  $\Delta E_g = 0$ , which is in contradiction with the experimental results for LiH<sub>x</sub>D<sub>1-x</sub> crystals. The change in  $E_g$  caused by isotopic substitution has now been observed for many broad-gap and narrow-gap semiconductor compounds. For example, the change of  $E_g$  for Cu<sub>2</sub>O [144]  $\Delta E_g = 18-25$  cm<sup>-1</sup>, for ZnO [126, 142]  $\Delta E_g = 12-55$  cm<sup>-1</sup>, and  $\Delta E_g = 110$  cm<sup>-1</sup> for diamond [127]. For comparison, let us recall once again that the change in  $\Delta E_g = 110$  cm<sup>-1</sup> for LiH is 103 meV (~ 831 cm<sup>-1</sup>). We see that the renormalization of  $E_g$  in LiH because of the isotopic effect is greater by an order of magnitude than that in diamond, although the width of the forbidden gap in diamond ( $E_g = 5.48$  eV,  $\hbar\omega_{\rm LO} = 0.165$  meV [147]) is larger than  $E_g$  in LiH. To end this section, let us note that  $E_g$  decreases by 97 cm<sup>-1</sup> when Li<sup>7</sup> is replaced with Li<sup>6</sup> (see Table 4).

4.3.2. Renormalization of the binding energy of Wannier-Mott excitons by the isotopic effect. It was in the very first work [23] where the binding energy of an exciton  $E_b$  was found to depend on the isotopic composition that this change in  $E_{\rm b}$  was attributed to the exciton – phonon interaction (in the first place, with the LO phonons). The preferential interaction of excitons with the LO phonons in LiH (LiD) crystals was later repeatedly demonstrated in the spectra of luminescence [5] and the RRLS [71], which consist of a phononless line (in the former case) and its LO repetitions (see Section 4.4). The effects of the Frohlich mechanism of the exciton - phonon interaction on the energy spectrum of Wannier-Mott excitons has been considered over and over again [21, 66, 72, 74, 99-102, 105, 106, 148]. Today we know that the main consequences of the interaction of electron and hole in an exciton with polarization vibrations are the static screening of the lattice charges (introducing  $\varepsilon_0$ ) and the change in the effective masses of particles. Both these effects of electron – (hole) – phonon interaction can easily be taken into account, and lead to the change in the exciton Rydberg  $E_{\rm b}$ . These corrections do not destroy the hydrogen-like structure of the exciton spectrum. At the same time, the non-Coulomb corrections to the electron - hole Hamiltonian modify the hydrogen-like structure - removing, for example, the degeneracy of levels with respect to the orbital and magnetic quantum numbers (see, for example, Ref. [74]). The very fact, however, that the problem of renormalization of the energy spectrum of the Wannier-Mott exciton does not admit an exact solution even in the limiting cases, often gives rise to a situation when there is no agreement between the results obtained by different authors. Starting with the classical works of Haken [21], all papers may be divided into two broad classes depending on how they account for the Coulomb interaction: between 'bare' electrons and holes, or between electrons and holes in the polaron state. In other words, first the interaction of band electrons and holes with the LO optical phonons is taken into account, and then the Coulomb interaction between electrons and holes clad in the 'polarization coats' is accounted for. As will be shown below, the study of the exciton – phonon interaction in crystals with the isotopic effect not only brings entirely new information, but also allows one to experimentally reconstruct the values of the Frohlich and Coulomb interaction constants. From Fig. 9 we see that when hydrogen is completely replaced with deuterium, the binding energy of the exciton exhibits a 20% increase from 42 to 52 meV [24]. It is easy to see that in the model of a virtual crystal the binding energy of an exciton in LiT crystals [155] must be 57 meV (see Fig. 9). Hence it follows that in the linear approximation the isotopic dependence of the binding energy of Wannier-Mott exciton

may be expressed as

$$E_{\rm b} = E_{\rm b}(0)(1+\gamma).$$
 (22)

where E(0) is the purely Coulomb binding energy of the exciton (in frozen lattice), which in our case is 31.5 meV, and the angular coefficient is  $\beta = 12.18 \text{ meV}/M$ , where *M* is the reduced mass of ions of lithium and hydrogen (deuterium, tritium);  $\gamma = \beta M/E_{b}^{(0)}$ . From the standard equation for the Coulomb binding energy of an exciton

$$E_{\rm b}(0) = \frac{e^4 \mu}{\hbar^2 \varepsilon_{\infty}^2} \tag{23}$$

we get the dimensionless constant of the Coulomb interaction:

$$\eta^2 = \frac{E_{\rm b}(0)}{\hbar\omega_{\rm LO}} = 0.47$$

Comparing the value of  $\eta^2 = 0.47$  and the constant of the Frohlich exciton – phonon interaction  $g^2 = 0.33$  [69] we see that they are close enough. This implies that both the Frohlich and the Coulomb interactions between electrons (holes) and LO phonons in an exciton must be treated with equal attention, as has already been emphasized in Ref. [105]. This paper deals from the start with 'bare' electrons and holes, and all renormalizations are calculated in the two-particle configuration. Such an approach permits the avoidance of a considerable difficulty which arises when polarons [151] are used as start-up particles. This difficulty is primarily associated with the fact that the momentum of each particle is conserved when the particles are treated separately, whereas it is the momentum of the center of mass that is conserved when a pair moves as a whole. As demonstrated in Ref. [105], this approach also makes it possible to calculate the higher-order corrections to the exciton - phonon interaction. It was also shown that the use of the pole parts of the Green polaron functions in place of complete expressions in Refs [150, 151] leads to a situation where the corrections to the potential energy of the order of  $\eta^2 g^2$  and  $g^4$  are lost because the corrections to the vertex parts and Green's functions cancel out. The quantity lost is of the same order  $(g^2)$  as the correction to the residue but has the opposite sign (for more details see Refs [150, 151]). The approach developed in Ref. [105] allowed the calculation of the corrections of the order of  $\eta^2 g^2$  and  $g^4$ ; the latter is comprised of the correction to the Frohlich vertex and the correction to the Green function in the exciton – phonon loop. It is important that the latter have opposite signs and exactly cancel out in the limit  $E_b \ll \hbar \omega_{LO}$ . As a result, because of the potential nature of the start-up Coulomb interaction, the correction to the Coulomb vertex of the order  $\eta^2 g^2$  does not vanish. As a result, the following expression was obtained in Ref. [105] for the binding energy  $E_{\rm b}$  of the Wannier-Mott exciton when  $E_{\rm b} \ll \hbar \omega_{\rm LO}$  (the spectrum of the exciton remains hydrogen-like):

$$E_{\rm b} = \hbar \omega_{\rm LO} \left[ \frac{\eta^2 - g^2 + \eta^2 g^2 (c+v)}{2} \right]^2, \tag{24}$$

where c,  $v = (m_{c,v}/\mu)^{1/2}$ , and  $m_c$ ,  $m_v$  are the masses of the electron and hole. Now  $E_b$  explicitly depends on  $g^2$  (the Frohlich constant of the exciton – phonon interaction), and hence depends on the isotopic composition of the lattice,

whereas the standard expression for the binding energy  $E_{\rm b} = \hbar \omega_{\rm LO} (\eta^2 - g^2) = e^4 \mu / 2\epsilon_0^2 h^2$ , which describes the exciton spectrum of many semiconductors accurately enough, exhibits no dependence on the isotopic effect. In the case of Eqn (24) the exciton spectrum remains hydrogen-like. When the higher-order corrections are taken into account, Eqn (24) becomes

$$E_{\rm b} = \frac{e^4 \mu}{2\epsilon_0^2 \hbar^2} \left[ 1 + g^2 \epsilon_0 \, \frac{c+v}{\epsilon_\infty} + g^4 \, \frac{\epsilon_0}{\epsilon_\infty} \right] \times \left( \xi_1 + \xi_2 \, \frac{1-\epsilon_\infty}{\epsilon_0} \right) (c+v)^2 \right].$$
(25)

The order-of-magnitude evaluation of the coefficients  $\xi_1$ ,  $\xi_2$  gives  $\xi_1 \approx 0.15$  and  $\xi_2 \approx 0.02$ ; when  $g^2(c+v) \ll 3.3$ , the correction of the order  $\eta^2 g^4$  is much less than the term of the order  $\eta^2 g^2$  [105]. So from Eqn (25) we see that the correction to the purely Coulomb binding energy (23) is important. This is primarily because the values of  $\eta^2$  and  $g^2$  are close to each other. Setting  $m_v/m_c = 3.5$  and  $g^2/\eta^2 = 1 - \varepsilon_0/\varepsilon_\infty$ , and  $(\varepsilon_\infty/\varepsilon_0) = (\omega_{\rm TO}/\omega_{\rm LO})^2 = 1/3.5$ , in Ref. [24] it was found that  $E_{\rm b(theor)} = 48$  and 42 meV for LiD and LiH respectively. Comparing these results with the experimental values (see Table 4) we observe a good agreement between theory and experiment. Hence follows a natural conclusion that the isotopic dependence of the binding energy of exciton is primarily due to the Frohlich mechanism of interaction between excitons and phonons.

In the preceding section it was mentioned that isotopic substitution affects not only  $E_b$ , but also  $E_g$ . For the system LiH – LiD at low temperatures the difference is  $\Delta E_g = 103$ meV. Apart from the zero oscillations considered in the previous section (see also Ref. [125], this change is also contributed to by the polaron shift which explicitly depends on the temperature. Figure 10 shows the temperature dependence of  $\Delta E = E_{n=1s}(\text{LiD}) - E_{n=1s}(\text{LiH})$ , which is generally similar to  $\Delta E_g \sim f(T)$ . From this diagram we see that as the temperature rises from 2 to 300 K, the quantity  $\Delta E$ decreases from 93 to 73.5 meV. The last figure agrees well with the value of 65 meV obtained in Ref. [34].

In the light of the Frohlich mechanism of exciton – phonon interaction considered above, the magnitude of the polaron shift may be estimated by the following expression:

$$\Delta E_{\rm pol} = -E_{\rm b}\hbar\omega_{\rm LO}\left(\frac{\varepsilon_0}{\varepsilon_\infty} - 1\right)\left(1 + c^2 + 1 + \frac{1}{v^2}\right).$$

This estimate gives about 20 meV [107], which is about  $1/4\Delta E$ ; on the other hand, it agrees well enough with the



Figure 10. Temperature dependence of polaron contribution to the change in  $E_g$  for isotopic substitution in LiH crystal.

magnitude of the polaron shift as derived from the temperature dependence of the shift (see Fig. 10).

Although the isotopic change in  $E_g$  has been observed for a large number of compounds (dielectrics and semiconductors), the number of studies of the isotopic effect on the exciton binding energy is limited to four cases. As demonstrated above, the replacement of a light isotope with a heavy one in LiH crystals [23] leads to an increase in  $E_b$ ; the binding energy decreases in CdS crystals and remains the same in the crystals of germanium [153] and diamond [127]. Quantitative measurements of the isotopic effect on the levels of largeradius excitons allow the experimental reconstruction of the Frohlich and Coulomb constants.

#### 4.4 Luminescence of free excitons in LiH crystals

Because of the low intensity of scattered light, and thanks to the high resolution of modern spectroscopic instruments, the development of highly sensitive techniques of detection of weak optical signals (photon counting mode, optical multichannel analyzers, optical linear arrays, and other specialized systems; see, for example, Ref. [154]), the luminescence method has become one of the most common techniques for studying excitons in dielectrics and semiconductors. While the structure of spectra of fundamental reflection (absorption) depends on the internal degrees of freedom of the Wannier-Mott exciton, the structure and shape of the luminescence spectrum are determined primarily by its external degrees of freedom. The latter are associated with the translation motion of a large-radius exciton as a whole, with translation mass  $M = m_{\rm e} + m_{\rm h}$ . [14]. The results on the luminescence (RRLS) of  $LiH_xD_{1-x}$  crystals presented below were obtained from the clean surface of crystals cleft directly under liquid superfluid helium in the cell of an optical cryostat [55]. The effects of surface habitus on the optical spectra (including the luminescence spectra) of excitons in hygroscopic LiH and LiD crystals were briefly described in Refs [55, 155, 156].

The luminescence of LiH crystals was first observed in 1959 [38]. The broad-band luminescence in the red part of the spectrum was attributed to defects related to the nonstoichiometric composition of the crystals (see also Refs [156, 157]). Later the broad-band luminescence of pure and activated (mostly with mercury-like ions with s<sup>2</sup> outer electron configuration [41]) LiH crystals was studied in a large number of works (see review [159] and references therein).

The first results on photoluminescence [160] of LiH crystals near the edge of fundamental absorption, like the first results on cathode-ray luminescence [161] were rather qualitative. The results on cathode-ray luminescence spectra of LiH crystals at 6 K are described in greater detail in Ref. [162]; they are analyzed and compared with the photoluminescence spectra in the review [159]. The LO repetitions were discovered in the spectra of X-ray luminescence of LiH crystals cleft in an inert gas environment [163]. The discovery of the LO structure of luminescence spectra and luminescence excitation spectra, and later that of RRLS [71] in LiH (LiD) crystals, has opened the opportunity for spectroscopic studies of processes of energy relaxation in the course of interaction with phonons [4].

As demonstrated earlier, the lowest-energy electron excitations in LiH crystals are the large-radius excitons. Exciton luminescence is observed when LiH crystals are excited in the midst of fundamental absorption [71, 75]. The spectrum of exciton photoluminescence of crystals of lithium

hydride cleft in liquid helium consists of a narrow (in the best crystals its halfwidth is  $\Delta E \leq 10$  meV [55, 57]) phononless emission line and its broader phonon repetitions, which arise due to radiative annihilation of excitons with the production of one to five LO phonons (Fig. 11). The phononless emission line coincides in an almost resonant way with the reflection line of the ground state of an exciton [56]. The lines of phonon repetitions form an equidistant series biased towards the lower energies from the resonance emission line of excitons. The energy difference between these lines, as before [163, 71, 4] is about 140 meV, which is close to the calculated energy of an LO phonon in the middle of the Brillouin zone [164] measured in Ref. [71]. The most important distinctions between the spectrum of exciton luminescence shown in Fig. 11 and the same measured earlier in Ref. [163] are the following: (a) the presence of a second series of the LO repetitions counted from the level of n = 2s exciton state; (b) comparable intensities of the phononless emission line and its 2LO repetition; (c) noticeable narrowing of the observed lines (see also Ref. [156]). Here we also ought to mention an overall increase in the intensity over the entire luminescence spectrum. Evidently, the intensity of the phononless emission line of free excitons (the proof of existence of quasimomentum is given below) increases because the rate of emissionless recombination on the surface decreases. This seems natural for the surface of a specimen cleft in liquid helium because the surface states (as a rule, of extrinsic origin [165, 166]) and their electric fields (recall that the value of the exciton Rydberg is relatively low,  $E_{\rm b} = 40$  meV) lead not only to broadening of the luminescence lines, but also to quenching of their intensity, and first of all, quenching of the intensity of phononless line.



Figure 11. Emission spectra of free excitons at 2 K in LiH crystals cleft in liquid helium. Spectral resolution of instrument is indicated on the diagram.

**4.4.1 Proof of the existence of quasi-momentum of excitons in LiH (LiD) crystals.** It is well known that one of the main properties of an exciton is its ability to move freely over the crystal lattice [14, 16]. In the approximation of effective mass [167], the exciton is regarded as a quasi-particle associated with a certain value of the wave vector (quasi-momentum) **k**, the changing of which characterizes the motion of exciton. The proof of motion of an exciton, especially in semiconductor crystals, has been the subject of many papers (see, for example, reviews [14, 16, 17, 66, 72, 100, 168, 169]). It was first demonstrated in Ref. [168] that an exciton in a crystal may

possess a considerable amount of kinetic energy. When the distribution of excitons is in equilibrium, the kinetic energy is known to be determined by the temperature of the crystal lattice. It is the studies of the line shapes and the temperature dependence of their relative intensity in the spectra of exciton – phonon luminescence that have supplied the most comprehensive information about the motion of excitons (and have proved this motion to be free), which allowed the establishment of the distribution law of excitons within the band [107]. Indeed, according to the law of conservation of quasimomentum, phononless emission is only possible for those excitons whose wave vector is of the same order of magnitude as the wave vector of the exciting photons ( $\mathbf{K} \cong 0$ ), and whose kinetic energy is practically zero. It is then that the phononless emission line is narrow. The emission processes, however, which are associated with the excitation of one or several optical phonons, may involve excitons with arbitrary values of kinetic energy and wave vector. In this case the excessive wave vector of thermal motion of an exciton is passed on to the phonons. Since the energy of optical phonons, as a rule, does not depend on the wave vector, the emission spectra will contain lines whose long-wave edges are displaced (see Fig. 11) by the energy of an integer number of optical phonons with respect to the energy of the ground state of phonon — the bottom of the exciton band (see also Ref. [169]). The shape of the emission lines, as indicated above, reflects the distribution of excitons with respect to their kinetic energy  $E_{kin}$ . Such an LO structure has actually been observed in the spectra of intrinsic luminescence of a large number of semiconductor crystals (see Refs [16, 14, 168, 170] and references therein). The shape of the LO phonon repetitions is described by the Maxwell distribution of excitons with respect to kinetic energy:

$$\frac{\mathrm{d}W}{\mathrm{d}E_{\mathrm{kin}}} = W E_{\mathrm{kin}}^{1/2} \exp\left(-\frac{E_{\mathrm{kin}}}{k_{\mathrm{b}}T}\right),\tag{26}$$

where W is the probability of an exciton – phonon interaction which depends on  $\mathbf{K}$  in the case of one-phonon scattering, and does not depend on  $\mathbf{K}$  in the case of two-phonon scattering [168, 170]. Figure 12 shows the comparison of an experimental first and second-order lines of exciton luminescence in LiH crystals with the shape described by Eqn (26). In general, the agreement between theory and experiment is reasonably good. At the same time, we notice that the halfwidth of the line is somewhat larger, and its shape on the long-wave side



**Figure 12.** Lineshapes of 1LO and 2LO repetitions in the exciton luminescence spectrum of LiH crystal at 62 K, and the Maxwell approximation of the distribution of excitons with respect to kinetic energy (dashed line) at 200 K.

differs from that described by Eqn (26). As will be shown below (see also Refs [159, 171]), this deviation is mainly determined by the magnitude of the longitudinal-transverse splitting — that is, by the strength of the exciton – phonon interaction [14, 178]. Reasonable accuracy in the description of the shape of the 1LO and 2LO repetitions may be achieved by assuming that the temperature of the exciton gas is 200 K [5]. This value is more than three times as high as the temperature of the crystal in the cryostat, which suggests that there is no thermodynamic equilibrium between the excitons and the lattice. This is one of the reasons why the emission lines of the LO repetitions in crystals cleft in liquid helium exhibit broadening even at the lowest temperature. This circumstance has already been noted in Ref. [55]. A detailed study of the temperature evolution of emission spectra of free excitons in LiD crystals [159] revealed a pronounced short-wave shift of the lines of the 1LO and 2LO repetitions with increasing temperature, which is obviously associated with the shift of the Maxwell distribution. This is a clear indication that excitons in these crystals do have kinetic energy. This conclusion fits in well with the results on the temperature dependence of the relative intensity of the 1LO and 2LO repetitions. In the temperature range where the distribution of excitons with respect to kinetic energy is in equilibrium, this dependence is well described by a linear function [103]. So we may conclude that the above results and their consistent interpretation indicate clearly that the observed emission is the emission of free excitons having a considerable amount of kinetic energy. Accordingly, the motion of excitons is coherent and complies with the law of conservation of quasi-momentum k.

4.4.2 Band relaxation of free excitons. Detailed information regarding the kinetic energy of free excitons can be extracted from the luminescence excitation spectra of free excitons [16, 173]. This function directly reflects the process of relaxation of excitons over the band. The important circumstance is that while the kinetic energy of excitons in the case of exciton phonon luminescence is usually of the order of kT, it can considerably exceed the binding energy of the exciton in the case of luminescence excitation spectra, as was first demonstrated in Ref. [173]. As an example, let us consider the exciton luminescence excitation spectrum (Fig. 13) in LiH crystals cleft in liquid helium. The most striking difference [156] between the results displayed in Fig. 13 and the excitation spectra of crystals cleft in hot air [4] is the presence of fine structure exactly in the exciton region. The observed structure of the excitation spectrum is related primarily to the manifestation of the n = 2s exciton state. In addition, the long-wave wing (see arrow 1 in Fig. 13) features a kind of 'singularity' at the distance of 8 meV.

This singularity may be related to the intervalley splitting [69], given the existence of three equivalent X valleys in the band structure of these crystals [68] where direct and allowed transitions take place [23]. As the kinetic energy of excitons increases, the observed structure smears out (for more details see Ref. [156]). This may be caused both by the reduced probability of indirect transitions in the course of absorption at large values of the wave vector [99, 174], and by the reduced probability of generation of excitons from recombination of electron – hole pairs [175–177]. The results presented in Fig. 13 lead to the conclusion that the excitons in these crystals (as well as in LiD [4]) may have very large kinetic energies (up to 0.5 eV). This is more than ten times their binding energy. Such



**Figure 13.** Excitation spectrum showing the emission line of the 2LO repetition in LiH crystal at 4.2 K, and the original record in the region of the ground and first excited exciton states.

a high value of the kinetic energy of excitons once again points to their high temperature, which fits in well with the large halfwidth of the phonon repetitions of exciton luminescence. The high velocity of these hot excitons ensures large travel paths within the crystal, thus facilitating their capture by the defects (impurities) of the LiH lattice. This apparently also explains the low quantum yield of luminescence of free excitons in these crystals ( $\eta \approx 3-0.1\%$  [5]). A similar structure consisting of the LO replicas is also displayed by the spectrum of excitation of emission lines of 1LO repetition (Fig. 14) in LiH crystals. As in the previous case (see Fig. 13), the highest intensity in the spectrum corresponds to the line removed from the emission line by the energy of 2LO phonons. The low intensity of the luminescence line of 1LO phonons did not allow the measurement of its spectrum over a broad range of energies. It is clear, however, that the intensity of the spectrum decreases and the lines broaden as the kinetic energy of excitons increases. In this way, accurate measurements of multiphonon luminescence spectra and excitation spectra of clean surface crystals allow one not only to demonstrate the existence of quasi-momentum of such excitons, but also to trace the band relaxation of excitons.



**Figure 14.** Original record of the excitation spectrum of the emission line of the 1LO repetition in LiH crystal at 4.2 K.

# 5. Isotopic effect in emission spectrum of polaritons

It is well known that when the photon – exciton interaction is taken into account, the intrinsic states of the crystal are represented by polaritons (see, for example, Ref. [20]). The energy range of polariton resonance is determined primarily by the strength of the oscillator, and is characterized by two quantities. The first of these is the energy  $E_{\rm T}$  corresponding to the bottom of the band of transverse mechanical excitons [15]. The second is the energy  $E_{\rm L}$  corresponding to the bottom of the band of longitudinal excitons which cannot be excited directly by transverse electromagnetic waves [14]. This approach allows us to say that there are two polariton branches above the energy  $E_{\rm L}$  in the energy spectrum of electron excitations: the lower polariton branch (LPB) and the upper polariton branch (UPB). The expedience of the polariton model for qualitative description of the experimentally observed features of resonance exciton emission was first demonstrated in Refs [178, 172]. Indeed, notwithstanding the successful theoretical description [66, 72] of the shape of emission lines in the LO repetitions and their relative intensities, the experimentally measured [179-183] halfwidth of the phononless emission line of free excitons and the relative intensity of phonon repetitions with respect to the phononless line do not fit in with the theoretical results for the model giving an equilibrium energy distribution of excitons. A characteristic feature of the observed manifestation of polariton effects in most non-metallic crystals is the doublet shape of the resonance luminescence lines of free excitons at low temperature [184, 185]. Today there is a huge body of experimental material on the luminescence of free excitons and its dependence on various factors, such as surface quality [180], the presence of defects created, for example, by gammaradiation [192], scattering by neutral and charged impurities [179], as well as reabsorption [180, 186] and the damping constant [187-191]. Moreover, while the theoretical interpretation of experimental results in Ref. [191] only involved kinetic effects on the energy distribution function, the description in Ref. [181] took into account both the energy and space distributions of polaritons. As a matter of fact, it is when not only the energy distribution but also the space distribution of polaritons is taken into account that a good agreement is achieved between theory and experiment. Thorough investigations of the shape of the phononless emission line in mixed  $A_2B_6$  crystals over a wide range of temperatures brought the authors of Ref. [192] to the conclusion that they were able to observe the polariton effects experimentally in these crystals (see also Refs [20, 15, 209]).

Figure 15 shows the luminescence spectra of LiH and LiD crystals, cleft and measured at 2 K. A more or less pronounced short-wave singularity of the phononless line is displayed by practically all crystals with clean surfaces [134]. The luminescence spectrum of LiD crystals shown in Fig. 15 (see also Ref. [4]) is largely similar to the spectrum of intrinsic luminescence of LiH crystals (see Fig. 11). There are, however, some distinctions: one is related to the unequal intensities of the phononless line (or, more precisely, of its long-wave component) and its 2LO repetition, whereas these intensities in LiH are practically the same. Another distinction is the clearly visible doublet nature of the phononless emission line of free excitons in LiD crystals even at a low temperature. On top of that, the magnitude of the long-



**Figure 15.** Luminescence spectra of LiD (a) and LiH (b) crystals cleft at 2 K and measured at 2 K. Insert: phononless emission line of free excitons at 78 K.

itudinal-transverse splitting for LiD is greater than for LiH, and constitutes  $25 \pm 2$  meV. A pronounced doublet structure of the phononless emission line with a magnitude of  $\Delta_{LT} = 18 \pm 2$  meV for LiH crystal is observed at an elevated temperature (Fig. 16). This value of  $\Delta_{LT}$  is somewhat larger than the magnitude of splitting observed in Ref. [185] using LiH crystal cleft in a jet of hot air. This behavior of  $\Delta_{LT}$  also agrees with the results of Ref. [180], where the surface quality was demonstrated to affect dramatically not only the structure but also the intensity of polariton luminescence. The measured value of  $\Delta_{LT} = 18$  meV for LiH crystals fits in well with the magnitude of splitting observed in the reflection [57, 50] and RRLS [57] spectra of clean surface crystals.

The doublet structure of the phononless emission line under consideration can be interpreted with the aid of the dispersion curve of polaritons. It is known (see, for example, Ref. [184]) that this curve represents a gradual transition from the dispersion of photons in the crystal  $E = \hbar ck$  to the dispersion curve of excitons  $E = E_0 + \hbar^2 k^2 / M$ , where k and M are the wave vector and the translation mass of the exciton. As was first shown in Ref. [193], it is this region, aptly referred to as a 'bottleneck', that is responsible for the processes of light absorption and emission by the crystal (see also Ref. [20]). According to this approach, the doublet structure of the phononless emission line is caused by the radiative decay of the states on the upper and lower polariton branches (the approximate locations of UPB and LPB are indicated in Figs 14 and 15 by arrows). As the temperature increases, the maximum of the energy distribution of polaritons in the crystal moves towards the higher energies, and the population of the UPB increases. According to the above, and as follows from Fig. 15, at T = 105 K the intensity of the shortwave component of the phononless emission line increases relative to the long-wave component. This result agrees well with the numerous data reported in the literature [20, 184, 194]. For a mixed crystal (x = 0.55), the emission spectrum



**Figure 16.** Luminescence of polaritons in LiH crystal cleft in liquid helium at 105 K (a) and 4.2 K (b).

also displays a similar doublet structure of the phononless emission line with a somewhat larger halfwidth than that in the original binary crystals (for more details see Ref. [171]).

Going back to the results displayed in Fig. 15 and looking at the magnitude of  $\Delta_{LT}$ , we see that it increases from 18 meV for LiH to 25 meV for LiD crystals. Since in the transition from LiH to LiD it is only the energy of LO phonons that is changed, one may assume that the main cause of renormalization of  $\Delta_{LT}$  is the change in the polariton – phonon interaction. With due account for the different values of  $E_{\rm b}$ (see Table 4) and for the dependence of  $\Delta_{LT}$  on the strength of the oscillator of the exciton transition [14], we may write  $\Delta_{\rm LT} \sim E_{\rm b}^2/E_{\rm g}$ . Substituting the values of  $E_{\rm b}$  and  $E_{\rm g}$  for LiH and LiD into this expression, we find that  $f^{(1)}_{(1)}(x^{(2)}) \sim c_{\rm c} c_{\rm c} c_{\rm c}$  with the expression of the second  $\Delta_{LT}^{(1)}/\Delta_{LT}^{(2)} = 0.65$  for LiH crystals. This is somewhat less than the experimental value of  $\Delta_{LT} = 25$  meV. This discrepancy (we estimate it at about 25%) may be caused by the polariton - phonon renormalization. Currently the mechanism of this renormalization is not clear, since the branches of acoustic phonons are practically unaffected by the isotopic substitution. On the other hand, since the energy of the LO phonons depends nonlinearly on the concentration of isotopes [195], one may expect that the dependence of  $\Delta_{LT}$  on the concentration of isotopes will also be nonlinear (see also Ref. [134]).

We see that the experimental material presented in this section gives convincing evidence that the magnitude of the longitudinal-transverse splitting of polaritons in LiH crystal increases as hydrogen is replaced with deuterium.

#### 6. Isotopic disordering of crystal lattice

According to the classical definition of Lifshits [196], there are two types of disordering in a crystal lattice: site disordering and structural disordering. In the first case we deal with the random distribution of atoms (ions) with different scattering properties in the lattice sites. Structural disordering is the distortion of the steric distribution of the lattice sites. Obviously, isotopic disordering ought to be classified as a site disordering of the crystal lattice. Even though a special volume has been published in a well-known series on solid state physics devoted to the optical properties of mixed crystals with different types of disordering [30] (and where, incidentally, the isotopic model is used — see, for example, Ref. [197]), there are simply no experimental results regarding the physical characteristics of isotopically mixed crystals. In this respect the present review is an important addendum to Ref. [30], since here we are mainly concerned with the description of experimental results and their consistent comparison with the existing theoretical models. Let us add that the fact that these effects are common for a large number of crystals (C, LiH, Ge) with different binding and different physical characteristics, permits us to find the limits of applicability of models over a broad range of microscopic parameters.

### 6.1 Effect of disordered lattice on the energy of interband transitions in $\text{LiH}_x\text{D}_{1-x}$ crystals

Numerous studies of reflection (absorption) spectra of mixed compounds A<sub>1</sub>B<sub>7</sub>, A<sub>2</sub>B<sub>6</sub>, and A<sub>3</sub>B<sub>5</sub>, carried out over the past four decades, point to the existence of large-radius excitons in these materials. The widths of exciton bands were shown to depend on the composition of the solid solution. The random relief of the potential is caused by disordering of the crystal lattice. According to modern views (see, for example, Ref. [197]), if the kinetic energy of an exciton exceeds the potential energy of localization, the exciton will not 'sense' the random relief of the potential. If the kinetic energy of exciton is small, then the exciton will be localized by the potential created by fluctuations of the composition of the crystal lattice. And since the energy of localization is different at different points of the sample, the energy of the exciton transition will also be different, which leads to broadening of the exciton line. The localized and delocalized states are separated by the mobility threshold [198]. From the above it becomes clear that exciton states in solid solutions will be observed when and only when the exciton is not ionized by the field of such a fluctuation, and broadening of the exciton lines is much less than the binding energy  $E_{\rm b}$  of the exciton in such states. In localized exciton states, not only is the relative motion of the exciton and hole localized, but also the translation motion of the exciton as a whole (see also Ref. [199]). It ought to be added that quasimomentum is no longer a good quantum number for excitons with low kinetic energy, and therefore excitons with different energies may be generated through the absorption of light. The density of states in the exciton band in the low-energy range is very different from the density of states of free excitons (Fig. 17). In Ref. [199] the method of optimal fluctuation (for more details see Ref. [196]) was used for finding expressions for the absorption coefficient k(E) in the region of the long-wave wing of the exciton line, as well as the density of the localized states  $\rho(E)$ . Both these functions fall off towards



Figure 17. Densities of states  $\rho(E)$  in exciton band for noncoherent and coherent motion of exciton. Dashed line shows the density of states for free excitons.

the bottom of the forbidden zone as

$$K(E) \propto \rho(E) \propto \exp\left(-\frac{E}{E_0}\right)^{1/2},$$
 (27)

where *E* is the energy of localization counted from the bottom of the exciton band in the virtual crystal model, and  $E_0$  is the parameter which defines the broadening of the exciton lines. It was demonstrated that the halfwidth of the exciton absorption line is  $14E_0$ . In chemically mixed semiconductor crystals, especially those of the  $A_2B_6$  group [197, 199], smearing of the edges of the conduction band and valence band occurs because of fluctuation of the electron potential; the band whose carrier is heavier is smeared more . Numerous comparisons of the results on broadening of exciton lines by large-scale composition fluctuations (whose geometrical size is comparable with the wavelength of the exciton) with the proposed theoretical model, point to good qualitative and quantitative agreement, especially for  $A_2B_6$  compounds (see Ref. [199] and references therein).

As follows from Fig. 8, excitons in  $\text{LiH}_x D_{1-x}$  crystals display a unimodal character, which facilitates the interpretation of their concentration dependence. Figure 18 shows the concentration dependence of the energy of interband transitions  $E_g$ . Each value of  $E_g$  was found by adding together the energy of the long-wave band in the reflection spectrum and the binding energy of the exciton. The latter was found from the hydrogen-like formula using the experimental values of the energies of levels of 1s and 2s exciton states. We see that the 100% replacement of hydrogen with deuterium changes  $E_g$  by  $\Delta E_g = 103$  meV at T = 2 K [133]. This constitutes 2% of the energy of electron transition, which is by two orders of magnitude greater than the value corresponding to isotopic replacement of atomic hydrogen with deuterium reported in Ref. [133].

The nonlinear concentration dependence of  $E_g$  can be sufficiently well approximated with a polynomial of the second order

$$E_{g}(x) = E_{b} + (E_{a} - E_{b} - b) x - bx^{2}, \qquad (28)$$

where  $E_a$ ,  $E_b$  are the values of  $E_g$  for LiD and LiH respectively, and b is the curvature parameter equal to 0.046 eV. This result generally agrees with the published data (see also Refs [200, 201] and references therein). For comparison let us indicate that in the case of isotopic substitution in germanium the energy  $E_g$  depends linearly on



**Figure 18.** Energy of band-to-band transitions  $E_g$  as a function of isotope concentration in mixed LiH<sub>x</sub>D<sub>1-x</sub> crystals at 2 K: *1* — linear dependence of  $E_g$  on x in the virtual crystal model; 2 — calculation according to Eqn (28); points derived from reflection spectra indicated by crosses, from luminescence spectra by triangles.

the concentration of isotopes for both direct ( $E_0$ ;  $E_0 + \Delta_0$ ;  $E_1 + \Delta_1$ ) and indirect [153] electron transitions. Unfortunately, at present there is no information on the form of the function  $E_g \propto f(x)$  for isotopic substitution in C, ZnO, CdS, Cu<sub>2</sub>O crystals, although, as noted above, the values of  $E_g$ have been measured for isotopically pure crystals (see Section 4.3.1).

#### 6.2 Broadening of lines of the exciton ground state in the spectrum of mirror reflection

As follows from Fig. 8, the addition of deuterium leads not only to the short-wave shift of the entire exciton structure (with different rates for 1s and 2s states [124]), but also to a significant broadening of the long-wave exciton reflection line. This line is broadened 1.5 to 3-fold upon transition from pure LiH to pure LiD. The measure of broadening was the halfwidth of the line measured in the standard way (see, for example, Ref. [203]) as the distance between the maximum and the minimum in the dispersion gap of reflection spectrum, taken at half-height. The concentration dependence of the halfwidth  $(\Delta E^{R})$  of the long-wave band in the exciton reflection spectrum at 2 K is shown in Fig. 19. Despite the large spread and the very limited number of concentrations used, one immediately recognizes the nonlinear growth of  $\Delta E^{\mathbf{R}}$  with decreasing x. A similar concentration dependence of  $\Delta E^{\mathbf{R}}$  in the low-temperature reflection spectra of solid solutions of semiconductor compounds A2B6 and A3B5 has been reported more than once (see, for example, the review [30] and references therein). The observed broadening of exciton lines is caused by the interaction of excitons with the potential of large-scale fluctuations of composition of the solid solution. Efros and colleagues (see, for example, Ref. [199]) used the method of optimal fluctuation [196] to express the formula for the concentration dependence of



**Figure 19.** Concentration dependence of halfwidth of the exciton ground state line in the mirror reflection spectrum at 2 K: I — approximation of the virtual crystal model; 2 — calculation according to Eqn (29); experimental points indicated by crosses.

broadening of exciton reflection lines:

$$\Delta E^{\mathbf{R}} = 0.5\alpha \left[ \frac{x(1-x)}{Nr_{\mathrm{ex}}} \right]^{1/2}.$$
(29)

where  $\alpha = dE_g/dx$ ; *N* is the concentration of sites which may be occupied by the replacement atoms;  $r_{ex}$  is the exciton radius which varies from 47 A to 42 A upon transition from LiH to LiD [133]. The value of coefficient  $\alpha$  was found by differentiating Eqn (28) with respect to x — that is,  $dE_g/dx = \alpha = E_a - E_b - b + 2bx$ . The results of the calculation according to Eqn (29) are shown in Fig. 19 by solid line.

The experimental results lie much closer to this curve than to the straight line plotted from the virtual crystal model. At the same time it is clear that there is only qualitative agreement between theory and experiment at x > 0.5. Nevertheless, even this qualitative analysis clearly points to the nonlinear dependence of broadening on the concentration of isotopes, and hence to the isotopic disordering. Since isotopic substitution only affects the energy of optical phonons, and as a consequence, the constant  $g^2$  of the exciton – phonon interaction (mainly the Frohlich one [69]), the nonlinearity of the functions  $\Delta E_g \propto f(x)$ ,  $\Delta E^R \propto f(x)$  is mainly related to the nonlinear behavior of  $g^2 \propto f(x)$ . In this way, the experimental study of the concentration dependence of the constant of the exciton – phonon interaction may throw light on the nature and mechanism of the large-scale fluctuations of the electron potential in isotopically disordered crystals.

## 6.3 Nonlinear dependence of binding energy on the isotope concentration

A matter of principle for further development of the theory is the question concerning the effect of crystal lattice disordering on the binding energy  $E_b$  of the Wannier–Mott exciton [149]. This problem has been treated theoretically in Refs [31, 33], where the effect of weak disordering on  $E_b$  was studied (the energy of disordering is comparable with  $E_b$  [31]). The binding energy in Ref. [31] was calculated in the approximation of a coherent potential by solving the Bethe–Salpeter equation as applied to the problem of the Wannier-Mott exciton in a disordered medium. One of the principal results of Ref. [31] is the nonlinear dependence of  $E_b$  on the concentration. As a consequence, the binding energy  $E_b$  at half-and-half concentrations is less than the value derived from the virtual crystal model. The binding energy of the exciton is reduced because the energy  $E_g$  is less, owing to fluctuation smearing of the edges of the conduction band and the valence band. This conclusion is in qualitative agreement (although not in quantitative agreement, the discrepancy being about an order of magnitude — see also Ref. [31]) with the experimental results for the mixed crystal GaAs<sub>1-x</sub> $P_x$ with x = 0.37, where the reflection spectra exhibited two exciton maxima (see also Fig. 8) used for finding the value of  $E_{\rm b}$  (see Refs [31, 136] and references therein). Let us add that the pivotal feature of the model of Ref. [31] is the shortrange nature of the Coulomb potential (for more details see Ref. [75]).

The data from Table 4 and other published sources [5, 124, 133] was used for plotting the energy  $E_b$  in Fig. 20 as a function of isotopic concentration x. The values of the binding energy  $E_b$  were calculated with the hydrogen-like formula (see below) using the energies of exciton levels of 1s and 2s states found from the reflection spectra (see Fig. 6). The theoretical description of the binding energy of Wannier-Mott excitons as a function of x was based on the polynomial derived in Ref. [31]:

$$E_{\rm b} = E_{\rm b}^{\rm crys} - E_{\rm bow} \left[ \frac{1 - W}{2U_0} \right] - E_{\rm eff} \,, \tag{30}$$

$$E_{\rm eff} = x(1-x)\frac{\delta_{\rm c}\delta_{\rm v}}{W}, \qquad (31)$$

$$E_{\rm b}^{\rm crys} = U_0 + \frac{W}{2U_0} - W_0 \,. \tag{32}$$

where  $W = W_c + W_v$ ; and  $W_c$  and  $W_v$  are the widths of the conduction and the valence bands which are 21 eV [88] and 6 eV [89] respectively. Here  $E_{\text{bow}}$  is the curvature parameter



Figure 20. Concentration dependence of the binding energy of the Wannier–Mott exciton: 1 — approximation of virtual crystal model; 2 — calculation according to Eqn (3); experimental points indicated by triangles.

found from the function  $E_g \propto f(x)$ ;  $\delta_c$  and  $\delta_v$  are the magnitudes of the fluctuation smearing of the edges of the valence and conduction bands,  $\delta_c = 0.103$  eV and  $\delta_v = -0.331$  eV. As follows from Fig. 20, these values of the parameters give a good enough description of the nonlinear dependence of the binding energy of the Wannier–Mott exciton in the disordered medium. This agreement between theory and experiment once again proves the inherent consistency of the model proposed in Ref. [31], since the isotopic substitution affects the short-range part of the interaction potential.

In this way, the nonlinear dependence of the binding energy of the Wannier–Mott exciton is caused by isotopic disordering of the crystal lattice.

### 6.4 Effect of disordering on linewidths of luminescence of free excitons

When light is excited by photons in the region of fundamental absorption in mixed  $LiH_xD_{1-x}$  crystals at low temperature, line luminescence is observed (Fig. 21), as in pure LiH and LiD crystals. As before [59], the luminescence spectrum of crystals cleft in liquid helium consists of the relatively narrow phononless line and its broader LO repetitions. For the sake of convenience, and without sacrificing generality, Fig. 21 only shows the lines of two LO repetitions. Usually up to five LO repetitions are observed in the luminescence (excitation) spectrum, as described in detail in Ref. [159]. In Fig. 21 we see immediately that the structure of all three spectra is the same. The difference is in the distance between the observed lines, as well as in the energy at which the luminescence spectrum begins, and in the halfwidths of the line. The first feature is explained by the gradual and smooth decrease of the energy of LO phonon upon transition from LiH to LiD. This is related to the unimodal nature of LO phonons in mixed  $\text{LiH}_x D_{1-x}$ crystals at high isotope concentrations (0.4 < x < 1.0 [195]). This conclusion was made in Ref. [195] from the spectra of RRLS. The second feature is attributed to the phonon renormalization (mainly through interaction with LO phonons [124]) of the energy of band-to-band transitions. The change in  $E_{\rm g}$  is also smooth and continuous though nonlinear (see Fig. 18). It is hard to miss the broadening of emission lines of excitons in mixed crystals as compared to pure crystals. This is especially clear for the lines of LO repetitions - as described earlier for mixed crystals of A<sub>2</sub>B<sub>6</sub> group in Ref. [204]. In our case the line broadening for some crystals is as large as three or four widths of the lines in pure crystals (see below).

A more detailed quantitative study of the lineshapes in repetitions was carried out using the example of a line in the 2LO repetition. The results of this study are presented in Fig. 22. Here curve *I* is the Maxwellian distribution of excitons with respect to kinetic energy [16]:  $I = WE_{kin}^{1/2} \exp(-E_{kin}/kT) dE_{kin}$ , where  $E_{kin}$  is the kinetic energy of excitons [see Eqn (26)]. Curve 2 is the result of convolution of the Lorentz and Gauss curves of the form (see, for example, Ref. [205]):

$$I_{\rm T}(E) = \int_{-\infty}^{\infty} I_{\rm F}(E') \exp\left[-4\ln 2 \frac{E'-E}{\delta^2}\right] dE', \qquad (33)$$

where  $I_F(E')$  is the Maxwell distribution of excitons, and  $\delta$  is the Gaussian broadening of the emission line due to the disordering of anions (isotopes) in the crystal lattice (see also Ref. [206]).



Figure 21. Emission spectra of free excitons light-excited in crystals of LiD (a),  $\text{LiH}_{0.45}\text{D}_{0.55}$  (b), LiH (c) at 4.2 K, cleft in liquid helium. Spectral resolution of instrument is indicated on the diagram.

Comparison of the calculated results with the experimental data clearly points (see Fig. 22) to a better agreement with curve 1. It is important that, as before [55], for reconciliation between theory and experiment one has to assume that the temperature of the excitons is 100 times greater than the temperature of the lattice<sup>†</sup>. Such large broadening can hardly be explained solely by third-order anharmonism, given the close values of the widths of branches of optical phonons in LiH and LiD [207]. Hence follows a reasonable assumption that some of the experimentally observed broadening is definitely caused by disordered isotopic substitution in the anion sublattice. An additional argument in favor of this assumption is the experimentally measured dependence of the halfwidth of the line of 2LO repetition on the concentration x shown in Fig. 23. Here also curve 1 represents the concentration dependence of the halfwidth of the line of 2LO repetition in the virtual crystal model — that is,  $\sigma = x\sigma_1 + (1 - x)\sigma_2$ , where  $\sigma_1$  and  $\sigma_2$  are the

†The existence of kinetic energy of heated excitons in mixed  $CdS_xSe_{1-x}$  crystals was recently reported in Ref. [204]. It ought to be noted that while the conclusion concerning the existence of quasi-momentum of free excitons made in Ref. [204] holds for small concentrations, in the case of  $LiH_xD_{1-x}$  the same is true for arbitrary concentrations of isotopes.



Figure 22. Photoluminescence spectrum of  $LiH_{0.21}D_{0.79}$  crystal at 4.2 K, cleft in liquid helium: *I* — Maxwell distribution calculated for the virtual crystal model; *2* — convolution of Lorentzian and Gaussian.



**Figure 23.** Concentration dependence of halfwidth of the luminescence line of the 2LO repetition in  $\text{LiH}_x D_{1-x}$  crystals cleft in liquid helium: *I* — approximation of the virtual crystal model; *2* — calculation according to Eqn (34); *3* — experimental points [133].

halfwidths of the lines of 2LO repetitions for pure LiH and LiD crystals. Although, as noted earlier, the change of the lattice constant of  $\text{LiH}_x\text{D}_{1-x}$  crystals with x is directly described by the virtual crystal model, from Fig. 23 we see that the linear approximation alone is not sufficient for describing the experimental dependence  $\sigma_{2\text{LO}} \propto f(x)$ . Much closer to the experimental results is curve 2, which is the result of calculation according to the model of Ref. [208]. In this model the dependence of  $\sigma_{2\text{LO}}$  on x is found with the aid of perturbation theory in the approximation of virtual crystal. The perturbation is represented by fluctuations of the crystal potential, which in Ref. [208] were treated according to the Lifshits method of optimal fluctuations [25]:

$$\sigma = 2 \left[ \frac{x(1-x)1.4 r_{\rm c}^3}{r_{\rm ex}^3} \right]^{1/2} \Delta \,, \tag{34}$$

$$r_{\rm ex} = xr_1 + (1-x)r_2, \quad \Delta = \frac{dE_{\rm g}}{dx},$$
 (35)

where  $r_c$  is the size of a cluster (fluctuation) (in the calculations the value of  $r_c$  was assumed to be equal to the lattice constant of mixed LiH<sub>x</sub>D<sub>1-x</sub> crystal [60]);  $r_{ex}$  is the

radius of an exciton in a mixed crystal found from Eqn (35);  $r_1$ and  $r_2$  are the exciton radii in pure crystals. The values of  $r_{ex}$ found from the hydrogen-like formula fit in with these values (see Sections 2.2 and 4.1). The dependence of the halfwidth of the emission line of free excitons in a mixed crystal on the composition of its lattice as calculated from Eqn (35) is also plotted in Fig. 23. Triangles on the same diagram depict the experimental points derived from the spectra of intrinsic luminescence of mixed  $\text{LiH}_x D_{1-x}$  crystals. Generally, there is a good enough agreement between theory and experiment. This agreement relates essentially to the nonlinear behavior of  $\sigma_{2LO} \propto f(x)$ . At the same time we see that the values of maximum  $\sigma$  in theory and experiment are not the same. The largest broadening of the line of 2LO repetition in  $\text{LiH}_x D_{1-x}$ crystal is experimentally observed at  $x \cong 40$  %. This, on the other hand, is in qualitative agreement with the results of Ref. [209] where the asymmetry of the function  $\sigma_{2LO} \propto f(x)$  is attributed to the fact that  $r_1$  and  $r_2$  are not the same. The common feature of the above results is also the maximum amount of broadening: three or four-fold according to both calculations and experiment. Notwithstanding the agreement between theoretical and experimental results, one must admit that it has not been possible to achieve quantitative agreement between the experiment and the model of Ref. [208]. We would like to emphasize, however, that the results of a quantitative study of the shape and halfwidth of emission lines of free excitons in mixed crystals described in this paper are, to our knowledge, presented for the first time. Further studies are certainly required to obtain the final form of the function  $\sigma \propto f(x)$ , which should take due account of the concentration dependence of anharmonism [210, 211]. Even these first results, however, obtained with a limited number of mixed crystals, are universal enough. Indeed, the existence of kinetic energy of excitons in mixed  $\text{LiH}_x D_{1-x}$  crystals (and hence the existence of quasi-momentum k) is another independent proof of importance of fine fluctuations of the potential for the localization of free excitons. The mismatch between the experimental results on the broadening of the emission lines of free excitons and the linear approximation of the virtual crystal model is a clear indication that it is necessary to take the lattice disordering into account even for isotopically mixed crystals [133]. We ought to add that

isotopic substitution in diamond [127], ZnO [125] and Ge [126, 212-214] also resulted in a shift of the luminescence spectrum of free excitons. Moreover, isotopic substitution in Ge leads not only to a shift of the luminescence spectrum, but also to the nonlinear concentration dependence of the half-width of the emission line, which, as in case of lithium hydride, was attributed to the isotopic disordering of the crystal lattice (see also Ref. [212]).

#### 7. Conclusions

The universality of a broad class of phenomena related to the isotopic effect on large-radius excitons in crystals with different structure and type of chemical bond (C, LiH, ZnO, CdS, Cu<sub>2</sub>O, Si, Ge) allows us to speak of a new emerging direction of research: the spectroscopy of Wannier-Mott excitons in crystals with different isotopic composition. Numerous practical applications of this research provide a strong and independent stimulus for its advancement. The existence of a large number of stable (or long-lived) isotopes, together with well-developed separation techniques, facilitate the development of isotopic engineering, which requires a deep understanding of the fundamental processes which take place in such compounds.

The experimental results presented in this review indicate that isotopic substitution of a light isotope by a heavy one leads to an increase in the band-to-band transitions with a nonlinear dependence on the concentration of isotopes, although the lattice constant of most isotopically mixed crystals (with the exception of diamond) complies with Vegard's law. A comparative study of the temperature and isotopic shift of the edge of fundamental absorption for a large number of different crystals indicates that the main (but not the only) contribution to this shift comes from the zero oscillations whose magnitude may be quite considerable and comparable with the energy of LO phonons. The replacement of light isotope by a heavier one causes a nonlinear increase in the binding energy of the Wannier-Mott exciton, and to an increase in the energy of longitudinal-transverse splitting the latter is especially hard to interpret theoretically. The theoretical description of the experimentally observed dependence of the binding energy of an exciton on the nuclear mass requires the simultaneous consideration of the exchange of LO phonons between the electron and hole in the exciton, and the separate interaction of carriers with LO phonons. Apart from the isotopic shift, all lines of the exciton spectra of reflection and luminescence (RRLS) exhibit additional broadening. The nonlinear concentration dependence of the energy  $E_{\rm g} \propto f(x)$  and the halfwidth of the long-wave exciton peak in the reflection spectrum  $\Delta E^{\mathbf{R}} \propto f(x)$  is caused primarily by isotopic disordering of the crystal lattice in mixed  $LiH_xD_{1-x}$  crystals. The nonlinear dependence of the binding energy  $E_{\rm g} \propto f(x)$  of Wannier–Mott excitons on the concentration  $x E_b \propto f(x)$  is due to fluctuation smearing of the edges of the conduction and valence bands. The experimental dependence  $E_b \propto f(x)$  for LiH<sub>x</sub>D<sub>1-x</sub> crystals fits in well enough with the calculations according to the model of large-radius exciton in a disordered medium; hence it follows that the fluctuation smearing of the band edges is caused by isotopic disordering of the crystal lattice.

The identical structure of spectra of intrinsic luminescence of pure crystals and mixed  $\text{LiH}_x D_{1-x}$  crystals, which consists of the narrow phononless line and its broader LO repetitions, and the peculiar temperature dependence of the intensity of these lines are definitely associated with emission by free excitons. Free excitons may carry kinetic energy which is as high as ten times their binding energy. The experimentally observed considerable broadening of the lines of LO repetitions in mixed crystals is also caused by isotopic disordering of the crystal lattice. A further argument in favor of the above is provided by the nonlinear dependence of the halfwidth of LO repetition in the emission spectrum of free excitons on the isotope concentration x. The observed dependence fits in qualitatively with the theory of the emission of excitons in disordered medium. It is also assumed that anharmonism of the third-order depends nonlinearly on the isotope concentration. We ought to emphasize the universality of phenomena associated with the isotopic effect and the effect of disordering in crystals of diamond, and lithium hydride, as well as silicon and germanium.

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