Direct observation of the effect of isotope-induced disorder on the exciton binding energy in LiH$_x$D$_{1-x}$ mixed crystals

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Abstract

The results of a quantitative study of the renormalization of the binding energy of the Wannier–Mott exciton by the isotope effect are presented for the first time. For this purpose, accurate measurements of the intrinsic luminescence and mirror reflection spectra of LiH$_x$D$_{1-x}$ mixed crystals with a clean surface in the temperature range 2–100 K were carried out. The nonlinear dependence of exciton binding energy $E_b$ on the isotope mass $E_b \sim f(x)$ is caused by the fluctuation broadening of the bands, which is connected with the isotope-induced disorder. The temperature dependence of the exciton binding energy is briefly discussed. The extrapolation of the asymptotic linear behaviour of the exciton maximum energy to $T = 0$ K enables us to estimate the zero-point renormalization of the exciton binding energy.

A wide variety of novel isotope effects have been discovered in the last four decades [1–6] owing to the availability of high-quality bulk semiconductor and insulator crystals with controlled isotopic composition (see, also, reviews [7–10]). Recent high-resolution spectroscopic studies of excitonic and impurity transitions in high-quality samples of isotopically enriched Si have discovered the broadening of bound exciton emission (absorption) lines connected with isotope-induced disorder as well as the dependence of their binding energy on the isotope mass [11–13]. The last effect was early observed on the bound excitons in diamond [14, 15], and earlier on the free excitons in LiH$_x$D$_{1-x}$ mixed crystals [16].

As is well known (see, for example [16, 17, 4]) the band gap energy $E_g$ in the $T \rightarrow 0$ limit has a dependence on the average isotopic mass $\overline{M}$ due to two effects: (a) the renormalization of $E_g$ by the electron–phonon interaction coupled with the dependence of the zero-point amplitudes on $\overline{M}$ (see also [18]); and (b) the dependence of the lattice constant on $\overline{M}$, leading to a change in $E_g$ through the hydrostatic deformation potential. The electron–phonon term is dominant [19, 20] and in the case of semiconductor crystals (C; Ge; Si) with a weak isotope scattering potential it varies approximately as $\overline{M}^{-1/2}$. The value of the $T = 0$ electron–phonon renormalization energy contribution to $E_g$ can be independently determined from an
extrapolation of the high-temperature linear dependence of $E_g \sim f(T)$ to $T = 0$, but again it should be remembered that $E_g \sim f(T)$ also has a small contribution from the change in204

In this communication we report the first results of a quantitative study of the dependence of the free exciton binding energy on isotope mass as well as on the temperature in LiH$_x$D$_{1-x}$ mixed crystals. We will show that the exciton binding energy increases by $10 \pm 1$ meV from $^7$LiH to $^7$LiD. Moreover, the dependence of $E_b \sim f(x)$ is nonlinear. The last effect, as will be shown below, is caused by the isotope-induced disorder of LiH$_x$D$_{1-x}$ mixed crystals. Part of these results has been published in brief in [21].

Specimens of LiH, LiD, LiH$_x$D$_{1-x}$ ($0 \leq x \leq 1$) and LiH$_x$F$_{1-x}$ were grown from the melt using the modified Bridgman–Stockbarger method (see also [22]). This technique has been described many times previously (see, e.g. [18, 2]). To improve the stoichiometric composition with respect to hydrogen (deuterium), the crystals grown were additionally annealed in an atmosphere of hydrogen or deuterium at a gas pressure of 3–5 atm, and a temperature of 500–550°C (the melting point is 961 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 [2, 7]).

Given the high reactivity of freshly cleaved 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 well-known method of cleaving directly in the helium chamber of an optical cryostat under liquid or superfluid helium, first tried in [23]. We did not notice any changes in the reflection or luminescence spectra while working for 10–16 h with surfaces prepared in this way. 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 cleaved off bulk high-quality crystals. The experimental setup for measuring the low-temperature reflection and luminescence spectra has been described more than once (see, e.g. [7, 18]) 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 cleaved, as described above, directly in the bath of the helium cryostat. The mirror reflection spectra were measured using an 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.

As demonstrated earlier (see, e.g. [7]) most low-energy electron excitations in LiH (LiD) crystals are large-radius excitons. The spectrum of exciton photoluminescence of LiH crystals cleaved in liquid helium consists of a narrow (in the best crystals, its half-width is $\Delta E \leq 10$ meV) phononless emission line and its broader phonon repetitions, which arise due to radiative annihilation of excitons with the production of one to five longitudinal (LO) phonons (see figure 1). The phononless emission line coincides in an almost resonant way with the reflection line (see the inset in figure 1) of the exciton ground state which is another indication of a direct electron transition ($X_1$–$X_4$ [2]). The lines of phonon replicas form an equidistant series biased toward lower energies from the resonance emission line of excitons. The energy difference between these lines is about 140 meV, which is close to the calculated energy of the LO phonon in the middle of the Brillouin zone [24] and which was measured in [19]. The isotopic shift of the zero-phonon emission line of LiH crystals equals that in reflection spectra, 103 meV (see, also, the inset in figure 1). As the deuterium concentration increases, the width of the long-wave maximum in the reflection spectra (and the width of the phononless line in the luminescence spectra) broadens, and the maximum shifts towards shorter wavelengths. As can
clearly be seen in figure 1, all spectra exhibit a similar long-wave structure. This circumstance allows us to attribute this structure to the excitation of the ground (1s) and the first excited (2s) exciton states [2]. Three distinct effects are shown in the reflection spectra by an increase in deuterium concentration:

1. the short-wavelength shift of the reflection (as luminescence) spectrum as a whole;
2. the different velocity shift of the exciton maximum of the ground and the first excited states on the temperature (see figure 2);
3. broadening of the long-wavelength maximum due to excitation of the ground exciton state.

We should note that the first excited exciton state is very clearly seen in the luminescence spectra too (see figure 3). Although two distinct contributions to $\Delta E_g$ (and respectively $E_b$) are present, due to the effect of the vibration on the lattice constant and the direct effect of the electron–phonon interaction [19, 20], for the present study of the dependence of the exciton binding energy on the isotope mass only the mechanism of exciton–phonon interaction will be considered.

In accordance with the second effect in reflection spectra (see above point 2), as is to be expected, there is a nonlinear dependence of the exciton binding energy ($E_b = 4/3\Delta_{12}$) on the isotope concentration. The curve displayed in figure 4 shows the Wannier–Mott exciton binding energy values, which are determined from the hydrogen-like expression $E_b = \frac{e^2 \mu}{2\hbar^2 n^2}$.
Figure 2. Temperature dependence of the distance between the long-wavelength peaks ($\Delta_{12}$) in specular reflection spectra of pure and mixed crystals. 1: LiH; 2: LiD; 3: LiD$_{0.995}$F$_{0.005}$.

Figure 3. The reflection (1) and luminescence (2) spectra of LiD crystal at 2 K.

using for this $E_1$ and $E_2$ values from the reflection and luminescence spectra (see figures 1 and 3). The nonlinear nature of this dependence is similar to the theoretical results [25], where the influence of the chemical disorder of the crystal lattice on the Wannier–Mott exciton binding
energy was seen and a qualitative (not quantitative!) agreement with experimental results on GaAs$_x$P$_{1-x}$ [26] mixed crystals obtained.

Before the comparison of our experimental results with the theory developed by Elliott and Kanehisa [25], it would be prudent to briefly review the main properties of their theoretical model. One of the principal results of [25] is the nonlinear dependence of the exciton binding energy $E_b$ on the concentration. As a consequence, the binding energy at half-and-half concentrations is less than the value derived from the crystal virtual model. According to [25] this model considers an exciton with a direct gap of a semiconductor alloy. Such a system consists of an electron (particle 1) in the conduction band ($c$) with mass $m_c$ and a hole (particle 2) in the valence band ($v$) with mass $m_v$. The problem of the exciton in disordered systems is to solve the Hamiltonian

$$H = \frac{\vec{p}_1^2}{2m_c} + \frac{\vec{p}_2^2}{2m_v} + u(\vec{r}_1 - \vec{r}_2) + V_c(\vec{r}_1) + V_v(\vec{r}_2),$$  \hspace{1cm} (1)$$

with both the Coulomb interaction $u$ and the potential $V_v$ due to disorder ($v = c, v$).

Reference [25] neglected disorder-induced interband mixing. As is well known, in place of the electron–hole coordinates, $(\vec{r}_1, \vec{p}_1)$ and $(\vec{r}_2, \vec{p}_2)$, one may introduce the centre-of-mass and relative coordinates, $(\vec{R}, \vec{P})$ and $(\vec{r}, \vec{p})$ to rewrite (1) as

$$H = \frac{\vec{p}_R^2}{2\mu_r} + u(\vec{r}) + \frac{\vec{P}^2}{2M} + V_c(\vec{R} + m_c\vec{r}/M) + V_v(\vec{R} - m_v\vec{r}/M),$$  \hspace{1cm} (2)$$

where $\mu_r$ and $M$ are the reduced and total masses of excitons, respectively. Because of the random potential, the translational and relative degrees of freedom cannot be decoupled. This is essentially difficult when considering the two-body problem in a disordered system (see [25] and references therein). However, when the exciton state in question is well separated from other states, so the energy spacing is much larger than the translational width and disorder, one can forget about the relative motion ($H_r = \frac{\vec{p}_r^2}{2m_r} + u(\vec{r})$) and just apply any single-particle alloy theory solely to their translational motion. For each exciton state the translational part of Hamiltonian in this case is

$$H_t = \frac{\vec{P}^2}{2M} + V_c(\vec{R}) + V_v(\vec{R}).$$  \hspace{1cm} (3)$$

Figure 4. Concentration dependence of the binding energy of a Wannier–Mott exciton at 2 K in LiH$_x$D$_{1-x}$ mixed crystals. 1: VCA approximation model; 2: calculation according to equation (8); experimental points are indicated by triangles.
Here $\bar{V}_c$ and $\bar{V}_v$ are averages of $V_c$ and $V_v$ with respect to the relative state $\phi$, for example:

$$
\bar{V}_c(\vec{R}) = \int d^3\vec{r} |\phi(\vec{r})|^2 V_c[\vec{R} + m v M].
$$

(4)

This approach is very similar to the Born–Oppenheimer adiabatic approximation. Such situations hold in some mixed alkali halide crystals and probably $A_2B_6$ crystals. In contrast, when the exciton binding energy is comparable to the disorder energy, the adiabatic approximation breaks down, and it is essential to take into account the effect of disorder on both the translational and relative motions. This is the case with the Wannier–Mott exciton in $A_3B_5$ alloys, for which the Elliott and Kanehisa model was developed. In this case the solution task is to start from the independent electron and hole by neglecting $u$ in (2) and then to take into consideration the Coulomb interaction between the average electron and average hole.

A further simplified approach adopted in the literature (see, for example, [27] and references therein) in solving the Bethe–Salpeter equation [28] is to suppose a free-electron-like one-particle Green’s function with a built-in width to allow for the random potential due to disorder. In the cited theoretical model [25], the average (or ‘virtual crystal’) gap is given by

$$
E_{vc}^g(x) = E_0 + (\delta_c - \delta_v)(x - 1/2),
$$

(5)

where $E_0$ is the average gap, and $\delta_c$ and $\delta_v$ are the values of the fluctuation broadening of the conduction and valence bands, respectively. Reference [25] also assumed the Hubbard density of states for both the conduction and valence bands with width $W_c$ and $W_v$, respectively, as well as similar dispersion in both bands. With this assumption the exciton binding energy has been calculated according to the coherent potential approximation CPA model. As is well known, the main idea of the coherent potential methods is in the introduction of an auxiliary medium with a regular, i.e., spatially periodic, potential. By definition in the model this potential is also complex. The formalism of the coherent potential model, convenient for performing calculation, does not include fitting parameters, because of use of the density of phonon states from the virtual crystal model which used the virtual crystal approximation (VCA). It should be added here that the key feature of the model developed in [25] is the short-range nature of the Coulomb potential (for details, see e.g. [7, 29]).

The data from figure 1 and other published sources [2, 7, 21] were used for plotting the energy $E_b$ as a function of isotopic concentration $x$ in figure 4. The binding energy (defined as the band edge minus the exciton energy) is given by [25]

$$
E_b^{\text{crys}} = U_0 + \frac{W}{2U_0} + W.
$$

(6)

In the last relation $U_0$ is the coupling constant at the total exciton momentum $\vec{q} = 0$.

The theoretical description of the binding energy of Wannier–Mott excitons as a function of concentration $x$ was based on the polynomial derived by Elliott and co-workers [25]:

$$
E_b = E_b^{\text{crys}} - E_{\text{bow}} \left[ \frac{1 - W}{2U_0} \right] - E_{\text{eff}},
$$

(7)

$$
E_{\text{eff}} = x(1-x)\frac{\delta_c \delta_v}{W},
$$

(8)

where $W = W_c + W_v$, and $W_c$ and $W_v$ are the widths of the conduction band and the valence band, which are equal to 21 eV [30] and 6 eV [31, 32] respectively. Here $E_{\text{bow}}$ is the curvature parameter found from the function $E_g \propto f(x)$ ($E_{\text{bow}} = 0.046$ eV [7]); $\delta_c$ and $\delta_v$ are the magnitudes of the fluctuation smearing of the valence band and the conduction band edges, $\delta_c = 0.103$ eV and $\delta_v = -0.331$ eV. As follows from figure 4, these values of the parameters give a good enough description of the nonlinear dependence of the binding energy.
of the Wannier–Mott exciton in disordered medium isotope-mixed crystals LiH, D1−x. This agreement between theory and experiment once again proves the inherent consistency of the model proposed by Kanehisa and Elliott, 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. As is seen from figure 4, the exciton binding energy decrease (relative linear law (VCA)—see the dashed line in figure 4) in the vicinity of the middle meaning concentration really draws attention to the fluctuated broadening of the edge of the conduction and valence bands. In accordance with the theoretical model, the last reason gives rise to the reduced $E_g$ and thereby the thinning of the exciton levels and, respectively, the reduction of $E_b$.

As follows from figure 1, 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), but also to a significant broadening of the long-wave exciton reflection line. This line is broadened 1.5–3-fold upon transition from pure LiH to pure LiD. The measure of broadening was the half-width of the line measured in the standard way (see e.g. [33]) as the distance between the maximum and the minimum in the dispersion gap of the reflection spectrum, taken at half-height. The concentration dependence of the half-width ($\Delta E_R$) of the long-wave band in the exciton reflection spectrum at 2 K is shown in figure 5. Despite the large spread and the very limited number of concentrations used, one immediately recognizes the nonlinear growth of $\Delta E_R$ with decreasing $x$. A similar concentration dependence of $\Delta E_R$ in the low-temperature reflection spectra of solid solutions of semiconductor compounds $A_3B_6$ and $A_5B_5$ has been reported more than once (see e.g. the review of Elliott and Ipatova [34] and references therein). The observed broadening of exciton lines is caused by the interaction of excitons with the potential of large-scale fluctuations in the composition of the solid solution. Efros and colleagues (see e.g. [35]) used the Lifshitz method of optimal fluctuation [36] to express the formula for the concentration dependence of the broadening of exciton reflection lines:

$$\Delta E_R = 0.5\alpha \left[ \frac{x(1-x)}{N_{\text{exc}}} \right]^{1/2}$$  \hspace{1cm} (9)
where \(N\) is the concentration of sublattices nodes where the isotope substitutes are placed; 
\[ \alpha = \frac{dE_g}{dx}; \] and \(r_{\text{ex}}\) is the exciton radius which varies from 47 to 42 Å upon transition from LiH to LiD [2]. The results of calculation according to equation (9) are shown in figure 5 by a full curve.

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 the optical phonon for the first time, and, as a consequence, the constant of exciton–phonon interaction (in the first place, the Fröhlich interaction \(g_F^2\)), the nonlinearity of functions \(\Delta E_b \propto f(x)\), \(\Delta E_R \propto f(x)\) is mainly related to the nonlinear behaviour of \(g_F^2 \propto f(x)\). In this way, the experimental study of the concentration dependence of the exciton–phonon interaction constant may throw light on the nature and mechanism of the large-scale fluctuations of the electron potential in isotopically disordered crystals.

Returning to the results of figure 2, let us add that the different temperature dependence of exciton peaks of the 1s and 2s exciton states leads to the temperature dependence of the binding energies of Wannier–Mott excitons

\[ E_b \sim f(T). \quad (10) \]

This problem has not received any adequate treatment. More specifically, the energy of the exciton binding \(E_b\) in LiH crystals (as well as in mixed crystals LiH\(_{1-x}\)F\(_{1-x}\) (LiD\(_{1-x}\)F\(_{1-x}\))) decreases with increasing temperature, whereas \(E_b\) increases for excitons of the green and yellow series in Cu\(_2\)O crystals [37]. A linear approximation of the exciton binding energy in LiD\(_{0.995}\)F\(_{0.005}\) (see curve 3, figure 2) representing \(E_b\) at \(T = 0\) K gives \(E_b(0) \approx 55\) meV. From this value we can see that renormalization of the binding energy by the zero-point vibrations equals approximately \(\pm 10\)% from this value; that is, on the other hand, it composes only half of renormalized exciton binding energy by the isotope effect (\(\pm 10\) meV, see above). It is not excluded that the other part of the renormalized exciton binding energy is caused by exciton–polar phonon interaction.

In conclusion, the exciton luminescence and reflection spectra are used in a quantitative study of the isotopic and temperature effects in LiH\(_{1-x}\)F\(_{1-x}\) mixed crystals with a clean surface. It was shown that the short-range character of the potential of a disordered crystal lattice with isotope substitution is responsible for the broadening of the valence and conduction bands. Nonlinear dependence of the exciton binding energy on the isotope mass \(E_b \sim f(x)\) is due the isotope-induced disorder of LiH\(_{1-x}\)D\(_{1-x}\) mixed crystals. The temperature dependence of the exciton binding energy has been briefly discussed. The extrapolation of the asymptotic linear behaviour of the exciton maximum energy to \(T = 0\) K enables one to estimate the zero-point renormalization of the exciton binding energy. Thus we can see that the effects of the zero-point vibration (\(T = 0\) K) are by no means negligible, and they result in the dependence of the exciton binding energy (bandgap \(E_g\)) on isotope mass at low temperature.

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