1 Isotope dependence of band-gap energy.

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Abstract. The results of the quantitative investigations of the renormalization of the absorption edge of different compounds by the isotope effect are described. The obtained dependence of the band gap energy versus isotope mass is in reasonable agreement with estimated value obtained from the temperature dependence of $E_g$ in LiH crystals. For the first time it was shown that the dependence $E_g = f(M)$ for the different materials has a parabolic character $\ln(\partial E_g/\partial M) = 6.105(\ln E_g)^2 - 7.870(\ln E_g) + 0.565$. Nonlinear character of this dependence may be indicated on the nonlinear dependence of the potential scattering on the isotope mass.

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Isotope substitution is a well-defined and easily controllable method to investigate intrinsic renormalization mechanisms of elementary excitations of solids. First of all, phonon frequencies are directly affected by changes of the average mass of the whole crystal or its sublattices (in the case of virtual crystal approximation) even when we look upon them as noninteracting particles, i.e. as harmonic oscillators. The renormalization of the fundamental electronic gap by electron-phonon interaction also depends on the isotope mass. Measuring the energy gaps in samples with different isotopic composition then yields the difference in the changes of the valence- and conduction-band renormalization.

In this communication we report the first results of the quantitative study the dependence of the band-gap energy on the isotope effect for different compounds. As was mentioned above isotopic substitution only affects the wavefunctions of phonons; therefore, the energy values of electron levels in the Schrodinger 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. It is for this reason the energy values of purely electron transitions in molecules of hydride and deuteride are found to be different (see, e.g. [1]). This effect is even more prominent when we are dealing with a solid [2]. This conclusion was confirmed on a qualitative level as early as the 1930s in Ref. [3]. Intercomparison of absorption spectra for thin films of LiH and LiD at room temperature revealed [3] that the longwave maximum (as we now know to be the exciton peak (see, e.g. [2])) moves 64.5 meV towards the shorter wavelengths when H is replaced by D. As will be shown below, this effect becomes even more pronounced at low temperatures.

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The mirror reflection spectra of mixed and pure LiD crystals cleaved in liquid helium are presented in figure 1. For comparison, on the same diagram we have also plotted the reflection spectra of LiH crystals with clean surfaces. All spectra have been measured with the same apparatus under the same conditions. As the deuterium concentration increases, the long-wave maximum broadens and shifts towards shorter wavelengths. As can clearly be seen in figure 1, all spectra
exhibit a similar long-wave structure. This allows us 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 2K are presented in Table I. The binding energies of excitons \( E_b \), calculated by the hydrogen-like formula, and the energies of interband transitions \( E_g \) (details see [4]) are also given in Table I.

The ionization energy, found from the temperature quenching of the peak of reflection spectrum [4] of the 2s state in LiD is 12 meV. This value agrees fairly well with the value of \( \Delta E_{2s} \) calculated by the hydrogen-like formula. Moreover, \( E_b = 52 \) meV for LiD agrees well with the energy of activation for thermal quenching of free-exciton luminescence in these crystals [2].

At the weak scattering potential the mean-square vibrational amplitude \(<u^2>\) of an atom depends on the phonon frequencies and the eigenvectors, the atomic masses (at low temperatures), as well as the temperature (at high temperature). Isotope substitution results in a slightly different vibrational amplitudes (especially at low temperature) and phonon frequencies and in first approximation equivalent to changing the temperature (see also [5]). The mass dependence of \(<u^2>\) becomes vanishingly small at temperature on the order or higher than the Debye temperature. Changes in either the isotope masses or temperature thus lead to changes in the band gap (see above Fig. 1) via the electron-phonon interaction, even at zero temperature in the case of mass changes. In general, the renormalization of the band gap [4] and its temperature dependence result from a complicated interplay of 1) first- and second-order electron-phonon interactions that contribute to the energy of conduction and valence bands; 2) changes due to thermal or isotopic lattice expansion, and 3) changes in the phonon occupation numbers (see [5] and references therein).

The dependence of the band gap energy on isotopic composition has already been observed for insulators and lowest (indirect-direct) gap of different semiconductors (see also [6]). It has been shown to result primarily from the effect of the average isotopic mass on the electron-phonon interaction, with a smaller contribution from the change in lattice constant. This simplest approximation, in which crystals of mixed isotopic composition are treated as crystals of identical atoms having the average isotopic mass is referred to as virtual crystal approximation (VCA) [7]. Going beyond the VCA, in isotopically mixed crystals one would also expect local fluctuations in the band gap energy from statistical fluctuations in local isotopic composition within some effective volume, such as that of an exciton. As follows from Fig. 1 excitons in LiH\(_x\)D\(_{1-x}\) crystals display a unimodal character, which facilitates the interpretation of their concentration dependence. Fig. 2 shows the concentration dependence of the energy of interband transition \( E_g \). As can be seen from Fig. 2 VCA method cannot describe observed experimental results. As will shown below this deviation from linear low (VCA approximation) is connected with isotope-induced-disorder in isotope mixed crystals LiH\(_x\)D\(_{1-x}\).

The temperature and isotopic mass dependence of a given energy gap \( E_g(T,M_i) \) can be described by average Bose-Einstein statistical factor \( n_B \) corresponding to an average phonon frequency \( \theta_i \) as (see also [5; 8]).
\[ E_g(T,M_i) = E_{bar} - a_r \left( \frac{M_{nat}}{M_i} \right)^{1/2} \left[ 1 + 2n_B \right], \quad (1) \]

where \( n_B = 1/\exp\left( \frac{\theta_i}{T} \right) - 1 \) and \( E_{bar} \) and \( a_r \) the unrenormalized (bare) gap and the renormalization parameter, respectively. In the low-temperature limit, \( T << \theta_i \), equation (1) reduces
\[ E_g(T,M_i) = E_{bar} - a_r \left( \frac{M_{nat}}{M_i} \right)^{1/2}, \quad (2) \]

Here \( E_g(T,M_i) \) is independent of temperature and proportional to \( (1/M_i)^{1/2} \), whereas \( a_r \) is the energy difference between the unrenormalized gap \( (M_i \to \infty) \) and the renormalized value [5].

In the high-temperature limit, \( T >> \theta_i \) and Eq. (1) can be written as
\[ E_g(T,M_i) = E_{bar} - 2T a_r \theta_i, \quad (3) \]

and \( E_g(T,M_i) \) is independent of \( M_i \) [5]. The extrapolation of Eq. (3) to \( T = 0K \) can be used to determine the unrenormalized gap energy \( E_{bar} \), i.e.,
the value that corresponds to atoms in fixed lattice position without vibrations (frozen lattice [4]), from the measured temperature dependence of \( E_g(T) \) in the high-temperature (i.e. linear in \( T \)) region.

Using Eq. (2) it can be written the difference in energy \( \Delta E_g \) between a given energy gap in isotopically pure material (LiH) and its isotope analogue (LiD)
\[ \Delta E_g = E_g(M_i) - E_g(M_{nat}) = a_r \left[ 1 - \left( \frac{M_{nat}}{M_i} \right) \right]^{1/2}, \quad (4) \]

As can be seen from Table 1 and results of [5] \( \Delta E_g \) at 2K equals \( \Delta E_g = 0.103 \text{ eV} \) and \( E_g(\text{LiH}, T = 0K) = 5.004 \text{ eV} \) (linear approximation and \( E_g(\text{LiH}, T = 300K) = 4.905 \text{ eV} \) then using Eq. (3) we obtain \( a_r = 0.196 \text{ eV} \). This magnitude is very close (approximately 84%) to the value of 0.235 eV of zero vibration renormalization of the energy band gap in LiH crystals (details see [4;5]). Using Eq. (4) we obtain \( \Delta E_g(\text{theor}) = 0.134 \text{ eV} \) that is very close, on the other hand, to observed experimental value equals 0.103 eV. The discrepancy between these values may be caused by the negligible contribution of the isotopic lattice expansion to the band gap renormalization.

The single-mode nature of the exciton reflection spectra of mixed crystals LiH\(_x\)D\(_{1-x}\) agrees qualitatively with the results obtained with the virtual crystal model (see, e.g. [7; 9]), being at the same time its extreme realization, since the difference between ionization potentials (\( \zeta \)) for this compounds is zero. According to the virtual crystal model, \( \zeta = 0 \) implies that \( \Delta E_g = 0 \), which in contradiction with the experimental results for LiH\(_x\)D\(_{1-x}\) crystals (details see, also [6]). In the light of obtained dependence \( E_g = f(T, M_i) \) for LiH\(_x\)D\(_{1-x}\) it is very interested to study such dependence for different materials. Although the details of the renormalization process of \( E_g \) are not known, observation of the isotope renormalization of \( E_g \) for many materials force to pay a great attention on this effect.

By now the change in \( E_g \) caused by isotopic substitution has been observed for many broad-gap and narrow-gap compounds. Below we briefly discuss the variation of the electronic gap (\( E_g \)) of different crystals with its isotopic composition. In the last decade the whole row of different semiconducting crystals was grown. These crystals are diamond [10], copper halides [11; 12], germanium [13;14], Si [8] and GaAs [15]. All enumerated crystals show the dependence of
the electronic gap on the isotope masses. It should be noted that the indicated effect (the variation of $E_g$ and $E_b$, see Table I and II) have maximum values in LiH crystals, although this effect in other crystals with isotopic composition are currently being reliably measured and investigated well. All numerated crystals show the dependence of the electronic gap on the isotope masses.

Before we complete the analysis of these results we should mention that before these investigations, studies were carried out on the isotopic effect on exciton states for a whole range of crystals by Kreingol’d and coworkers [16-21]. First of all we should name the classic crystals Cu$_2$O [17-19] with the substitution O$_{16}^\rightarrow$O$_{18}$ and Cu$_{63}^\rightarrow$Cu$_{65}$. Moreover, there have been some detailed investigations of the isotopic effect on ZnO crystals [6] where $E_g$ was seen to increase by 55 cm$^{-1}$ (O$_{16}^\rightarrow$O$_{18}$) and 12 cm$^{-1}$ (at Zn$^{64}^\rightarrow$Zn$^{68}$) [16,20]. In the paper of Kreingol’d and coworkers [21] it was shown that the substitution of a heavy S$^{34}$ isotope for a light S$^{32}$ isotope in CdS crystals resulted in a decrease in the exciton Rydberg constant ($E_b$).

More detailed investigations of the exciton reflectance spectrum in CdS crystals were done by Zhang et al [22]. Zhang et al to directly determine the binding energy ($E_b$) and the corresponding band gaps ($E_g$) from a hydrogenlike model.

In this manner it was obtain binding energies of A excitons of 26.4±0.02 meV and 26.8±0.02 meV in $^{112}$CdS and $^{nat}$CdS, respectively. The corresponding band gaps $E_g(\Gamma_c - \Gamma_9)$ are 2.5806(2) eV and 2.5809(2) eV, respectively. In the case of B excitons, these values are $E_b = 27.1±0.2$ meV (27.1±0.2 meV) and $E_g (\Gamma_c - \Gamma_7) = 2.5964(2)$ [2.5963(2) eV] for the $^{112}$CdS [*$^{nat}$CdS] sample. Unfortuntealy, the n = 2 excited states of the A and B excitons could not be observed in other isotopic CdS samples. Better samples are required for such measurements.

For GaAs or ZnSe, isotope substituents of either type should lead to shifts of the $E_0$ gap which have been calculated to be 430 (420) and 310 (300) µeV/amu for cation (anion) mass replacement, respectively [15,23]. These values are in reasonable agreement with data measured for GaAs [*$\partial E_0/\partial M_{Ga} = 390 (60) \mu eV/amu$] and preliminary results for isotopic ZnSe obtained by Zhang et al [22] based on photoluminescence measurements of the bound exciton (neutral acceptor I$_1$) [*$\partial E/\partial M_{Se} = 140 \pm 40 \mu eV/amu$ and $\partial E/\partial M_{Zn} = 240 \pm 40 \mu eV/amu$].

Such behavior, however, is not found in wurtzite CdS. A previous reflectivity and photoluminescence study of $^{nat}$CdS$^{32}$S and $^{nat}$CdS$^{34}$S shows [21] that for anion isotope substitution the ground state (n = 1) energies of both A and B excitons have a positive energy shift with the large rate of $\partial E/\partial M_{Cd} = 740 \pm 100$ µeV/amu. This value is more than one order of magnitude larger than $\partial E/\partial M_{Cd}$ obtained by Zhang et al [22].

Several groups have conducted low-temperature studies of the direct and indirect band gaps of natural and isotopically controlled Ge single crystals. For the first time Agekyan et al [13] used photoluminescence, infrared absorption, and Raman spectroscopy with a Ge crystals of natural composition and a crystals with 85 % $^{76}$Ge and 15% $^{74}$Ge. They found an indirect band-gap change $\Delta E_g = 0.9$ meV and a direct band-gap change $\Delta E_g = 1.25$ meV with an error of ±0.05 meV. Etchegoin et al [24] and Davies et al [25] reported photolumi-
nescence studies of natural and several highly enriched, high quality single
crystals of Ge. Measurement of the energies of impurity-bound excitons per-
mits by Davies et al. the direct determination of band-gap shifts with the crystal
isotope mass because the radiative recombination does not require phonon par-
ticipation. As may be expected from the very large Bohr orbit of the excitons
(see Davies et al. [25] and reference therein), their binding energy only depends
on the average isotope mass and not on the isotopic disorder (see, however [4]).
The rate of band-gap energy change with isotope mass as determined by Davies
et al. is $dE_{IG}/dA = dE_{NP}/dA = 0.35\pm 0.02$ meV/amu. Etchegoin et al. [24]
obtained a very similar value.

Zollner et al. [25] have performed a numerical calculation of the electronic
bands using an empirical pseudopotential method including the necessary lat-
tice dynamics. They found for Ge $(dE_{IG}/dA)_{\mathrm{e-p}} = 0.41$ meV. The total calculated
shift of the indirect band-gap energy with isotope mass adds up to
$(dE_{IG}/dA)_{\text{total}} = 0.48$ meV. This result compares favorably with the experi-
mental values stated above by Davies et al. and by Etchegoin et al. who reported
$(dE_{IG}/dA)_{\text{total}} = 0.37\pm 0.01$ meV/amu.

Measurements of the direct band gap at the $\Gamma$ point ($\vec{k} = 0$) in the Brillouin
zone have also been performed. Though the direct band gap is technologically
less important than the minimum indirect band gap, determining the dependence
of this gap on isotope mass is of the same fundamental significance as the indi-
rect band-gap studies. Davies et al. [27] used low-temperature optical-absorption
measurements of very thin samples of Ge single crystals with natural composi-
tion and three different, highly enriched isotopes. They found $dE/dA = 0.49$
$\pm 0.03$ meV/amu for the temperature extrapolated to zero. Parks et al. [28]
have used piezo- and photomodulated reflectivity spectra of four monoisotopic
and one natural Ge crystals. These techniques do not require the extreme sam-
ple thinning which is necessary for optical-absorption measurements and the
derivative nature of the spectra emphasizes the small changes. The excellent
signal-to-noise ratio and the superb spectral resolution allowed a very accurate
determination of the dependence of $E_{DG}$ on isotopic mass. At very low
temperatures an inverse square-root dependence accurately describes band-gap
dependence $E_{DG} = E_{DG}^\infty + C \sqrt{M}$.

A fit through five data points yields $E_{DG}^\infty = 959$ meV and $C = -606$ meV/amu$^{1/2}$.
Written as a linear dependence for the small range of isotopic masses, Parks et
al find $dE_{DG}/dA = 0.49$ meV/amu, in perfect agreement with the results
of Davies et al. [27]. Parks et al. also determined the isotope mass dependence
of the sum of the direct gap and the split-off valence band ($\Delta_0$) and find $d(E_{DG} +
\Delta_0)/dA = 0.74$ meV/amu. The experimental results can be compared to
the Zollner et al. [26] calculations which are found to be of the correct order of
magnitude. The theoretical estimates for the contributions of the linear isotope
shifts of the minimum, indirect gaps which are caused by electron-phonon in-
teraction, are too large by a factor of $\sim 1.7$ and for the smallest direct gap they
are too large by a factor $\sim 3.2$.

Substitution of Ga$^{70}$ on the Ga$^{76}$ increases the band gap in GaAs [23] on
The interested results were communicated in papers of Cardona and coworkers [15; 12], where it was studied the dependence of \( E_g \) on the isotope effect in CuCl crystals. When the Cu\(^{64}\) on the Cu\(^{65}\) is substituted the value of \( E_g \) in CuCl crystals decreases on 1.24 cm\(^{-1}\), e.g. the isotope effect on the electronic excitation has an opposite sign.

Considering the series of Ge, GaAs, ZnSe, CuBr, for example, the 3d states of the first constituent play an increasing role in determining the band structure. In Ge these states can be considered as localized core states (atomic energy level \( \approx -30 \) eV). Already, however, in GaAs they have moved up in energy by 10 eV, and their hybridization with the top of the valence band affects the gap. Proceeding further in the series, this effect becomes more important, and in CuBr and Cu 3d states even overlap in energy with halogen p-states, with which they strongly hybridize. Therefore, we cannot exclude that the main reason for the opposite sign of the isotopic effect in these compounds may be connected to the different character of the d-electron-phonon interactions in these semiconductors [6].

Analogous investigations of the direct absorption edge of Si (\( E_g = 3.562 \) eV) have been performed in paper [8] made the value of the coefficient \( \partial E_g / \partial M = 2.0 \) meV/amu. The measurements of \( \partial E_g / \partial M \) for isotope effect in CsH (CsH\( \rightarrow \)CsD) gave the value \( \partial E_g / \partial M = 60 \) meV/amu [29]. The change of the indirect gap of diamond between pure C\(^{12}\) and C\(^{13}\) has been determined by Collins et al [10], using for this purpose the cathodoluminescence spectra of diamond. From the results of Collins et al it was concluded that the dominant contribution arises from electron-phonon coupling, and that there is a smaller contribution due to a change in volume of the unit cell produced by changing the isotope. These two terms were calculated as 13.5 \( \pm \) 2.0 and 3.0 \( \pm \) 1.3 meV respectively (details see, also [30]).

All of these results are documented in Table II, where the variation of \( E_g \) and \( \partial E_g / \partial M \) are shown at the isotope effect. We should highlight here that the most prominent isotope effect is observed in LiH crystals, where the dependence of \( E_g = f ( C_H ) \) is also observed and investigated (see, also [2]). Using the least-squares method it was found the empirical dependence of \( \ln(\partial E_g / \partial M) \sim f(\ln E_g) \), which is depicted on Fig. 3. As can be seen the indicated dependence has a parabolic character:

\[
\ln(\partial E_g / \partial M) = 6.105(\ln E_g)^2 - 7.870(\ln E_g) + 0.565. \quad (5)
\]

From this figure it can be concluded also that the small variation of the nuclear mass causes the small changes in \( E_g \) also. When the nuclear mass increases it causes the large changes in \( E_g \) (C: LiH; CsH) [30]. Moreover as can be seen from Fig. 3 in last case the empirical dependence \( \ln(\partial E_g / \partial M) \sim f(\ln E_g) \) is very close to the linear one and in ordinary coordinate system it has a next expression:

\[
\sqrt{\partial E_g / \partial M} = E_g^{6.105} (\partial E_g / \partial M = E_g^{3.0525}). \quad (6)
\]

By the way it should be noted that at the large changes \( E_g \) result in the changes of the force constants at the isotope effect from the large variation of nuclear mass. Observable in Fig. 3 rather large scattering data in the rate of change \( E_g \) on the isotope mass in the first step cause the different degree of the isotope-induced-disorder. The
last effect, as is well-known (see e.g. [4]), due the different magnitude of the
scattering potential at the isotope substitution.

We conclude the discussion of the band-gap shifts with isotope mass by ob-
serving that the effects are exceedingly small in the most cases (see Table 2)
and most likely will not have any consequences any semiconductors technolog-
ical applications. However, this exercise is an excellent demonstration of the
advanced state of our quantitative theoretical understanding of the subtle effects
of temperature, pressure and isotope mass on the electronic band structure.

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1.0.2 References

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1.0.3 Figure Captions.

Fig. 1. Mirror reflection spectra of crystals: LiH, curve 1; LiH$_{0.82}$D$_{0.18}$, curve 2; and LiD, curve 3 at 4.2 K. Light source without crystal, curve 4. Spectral resolution of instrument indicated in the diagram. All curves have the same energy scale.

Fig. 2. Dependence of the interband transition energy $E_g$ in mixed LiH$_x$D$_{1-x}$ crystals on the hydrogen concentration $x$. The straight dashed line is the linear dependence $E_g = f(x)$ in the virtual crystal model. The solid line corresponds to calculations using the polynomial of second degree [2] Points derived from reflection spectra indicated by crosses, and those from luminescence spectra by triangles.

Fig. 3. The dependence of $\ln(\partial E_g/\partial M) \sim f(\ln E_g)$; points are experimental data from Table 2 and continuous line - calculation on the formula (5).

Table 1. Values of the energy of maxima in exciton reflection spectra of pure and mixed crystals at 2K, and energies of exciton binding $E_b$, band-to-band transitions $E_g$.

| Energy, meV | LiH | LiH$_{0.82}$D$_{0.18}$ | LiH$_{0.40}$D$_{0.60}$ | LiD | Li*H (78K) |
|-------------|-----|----------------------|----------------------|-----|-------------|
| $E_{1s}$    | 4950| 4967                 | 5003                 | 5043| 4939        |
| $E_{2s}$    | 4982| 5001                 | 5039                 | 5082| 4970        |
| $E_b$       | 42  | 45                   | 48                   | 52  | 41          |
| $E_g$       | 4992| 5012                 | 5051                 | 5095| 4980        |

Table 2. Values of the coefficients $\partial E/\partial M$ (meV) and energies of the band-to-band transitions $E_g$(eV) according to indicated references.
| Substance          | $\partial E_g/\partial M$ (meV) | $E_g$ (eV)         |
|-------------------|---------------------------------|-------------------|
| $^{13}$C→$^{12}$C | 14.6 [10]                       | 5.4125 [10]       |
| $^7$LiH→$^7$LiD    | 103 [2,4]                       | 4.992→5.095 [2,4] |
| $^7$LiH→$^6$LIH    | 12 [5]                          | 4.980 [2,4]       |
| CsD→CsH           | 60 [29]                         | 4.440 [29]        |
| $^{30}$Si→$^{28}$Si| 2 [8]                           | 3.652 [8]         |
| $^{68}$ZnO→$^{64}$ZnO| 0.372 [16,20]             | 3.400 [16,20]     |
| Zn$^{18}$O→Zn$^{16}$O| 3.533 [16,20]             | 3.400 [16,20]     |
| $^{65}$CuCl→$^{63}$CuCl| -0.076 [11,12]             | 3.220 [11,12]     |
| Cu$^{37}$Cl→Cu$^{35}$Cl| 0.364 [11,12]             | 3.220 [11,12]     |
| Cd$^{34}$S→Cd$^{32}$S| 0.370 [21]                     | 2.580 [21]        |
| $^{110}$CdS→$^{116}$CdS| 0.040±0.068 [22]         | 2.580 [22]        |
| Cu$^{18}$O→Cu$^{16}$O| 1.116 [17-19]                | 2.151 [17-19]     |
| $^{71}$GaAs→$^{69}$GaAs| 0.39 [15]                   | 1.53 [15]         |
| $^{76}$Ge→$^{72}$Ge| 0.225 [13]                     | 1.53 [13]         |
| $^{76}$→$^{73}$→$^{70}$Ge| 0.37 [24-28]              | 0.74 [24-28]      |