PHYSICAL REVIEW B VOLUME 54, NUMBER 6 1 AUGUST 1996-II

Isotope-induced energy-spectrum renormalization of the Wannier-Mott exciton in LiH crystals

V. G. Plekhanov
International University ''LEX'', Uus Street 19, EEOOO1, Tallinn and Fonoriton Science Laboratory, Garon Ltd.,
P.O. Box 2632, EEOO38, Tallinn-38, Estonia

(Received 3 January 1996; revised manuscript received 29 April 1996)

The results of the quantitative investigations of the renormalization of the energy spectrum of the Wannier-Mott exciton by the isotope effect are presented. For this purpose accurate measurements of the mirror reflection and intrinsic luminescence spectra of $\mathrm{LiH}_x\mathrm{D}_{1-x}$ mixed crystals with a clean surface were carried out at a low temperature. The results of the experiment showed that the isotope substitution of the light isotope by the hard one increased the exciton binding energy E_b as well as the energy of the polariton longitudinal-transversal splitting. Nonlinear dependence $E_b \sim f(x)$ is due primarily to the fluctuation broadening of the valence and conduction bands and is described by the second degree of the polynom. This broadening is connected with the isotope disorder of the crystal lattice. The reasons for nonlinear dependence of $\Delta_{\mathrm{LT}} \sim f(x)$ are briefly discussed. This emphasizes that the control of the isotope constitution of the crystal lattice makes it possible to create systems with variable effectiveness of exciton(polariton)-phonon interaction. It is shown that the quantitative investigation of such systems permits the experimental reconstruction of the Coulomb and Frochlich value couplings. [S0163-1829(96)04230-0]

I. INTRODUCTION

The discovery of the isotope composition matter demanded a fundamental reexamination of the quantum mechanics foundation. In particular, the theoretical description of the experimental results on the spectroscopy of the molecules with the isotope composition was necessary to introduce to the quantum theory not only half-integer but also zero-point vibrations. Zero-point vibration energy is different for ground and excited electron states and depends only on the isotope mass. It cannot be changed by any external action. The different meanings of zero-point vibration energy for different isotopes causes a shift of the pure electron transition in molecules with different isotope compositions. Although the electron terms of the molecules do not depend directly on their isotopes compositions, they are nevertheless variable for molecules with different isotopes. This difference determines first of all their reconstruction of the electron-vibration interaction. The quantitative dimension of this difference can serve as the nonadiabatic degree. The electron-lattice interaction coupling depends on the vibration frequency and thus on the isotopes. Simultaneously it was noticed that for the description of the isotope shift of the pure electron transition in molecules (e.g., hydrides) the harmonic approximation of the theory turned out to be insufficient (see, e.g., Ref. 1). The successful study of the isotope effect in the atomic spectroscopy had already brought the conclusion about the two contributions to the energy shift of the atomic levels. The first one is connected to the dependence on the nuclear mass and the second is due to the field contribution.[2]

A large amount of the stable and long-lived isotopes enables us presently to talk about the spectroscopy of isotope mixed crystals. The well-developed modern technology of the isotope separation makes it possible to receive the high pure materials with practically 100% homogeneous composition on the different isotopes. Not only for the fundamental investigations, but for the applied tasks, were grown crystals of diamond, lithium hydride, $\mathrm{Cu_2O}$, Ge, and Si with different isotope composition. There are successful investigations into the dependence of crystal lattice dynamics on isotope composition in diamond,[3] LiH,[4] and Ge (Ref. 5) crystals. Despite the different degree of longitudinal-optical (LO) phonons scattering in C, Ge (weak), and LiH (strong) crystals the changeable LO phonon energy, in accordance with the theory, was common for all these crystals. From this fact it followed that the isotopical substitution primarily changes the Frochlich electron-phonon interaction. Consequently, the isotope substitution should cause a change of band-gap energy value (E_g), and, thus, the optical spectrum of the solid state. This qualitative conclusion corresponds very well with the experimental results of Ref. 6. In Ref. 6 on the thin-film absorption spectra it was shown that the substitution of H on D in LiH, the short-wavelength shift, the most long-wavelength (actually, excitons) peak was observed. The value of the shift is equal to 65 meV (Ref. 6) at room temperature and 103 meV at liquid-helium temperature.[7] After that an analogous change of the E_g value was observed in $\mathrm{Cu_2O}$,[8] ZnO,[9] and CdS (Ref. 10) at the isotope substitution both in cation and anion sublattices. Recently analogous results were obtained in germanium[5,11] as well as diamond.[12] The experimental manifestation of the dependence E_g on the isotope composition of the crystals[13] is analogous to that in the chemically mixed crystals (see, e.g., Ref. 14). However, from a theoretical point of view the description of the dependence E_g on the isotope composition is more simple than in the case of the chemically mixed crystals. The point is that in the isotope mixed crystals only the phonon wave function is changed whereas in the second case the phonon as well as the electron wave functions are changed. It is possible to conclude that the isotope mixed crystals could be a focus of interest as model objects for the investigations of the optical characteristics of chemically mixed crystals. The last remark is likewise related to the exciton states in the mixed crystals.

The well-developed exciton structure in the optical spectra of Cu_2O, CdS, ZnO, and LiH crystals allows us to conduct investigations into the dependency of the energy characteristics of the excitons large radius on the isotope composition. Taking into account the scarcity of experimental results, similar results could appear as an additional test for the modern theory of the Wannier-Mott excitons in mixed crystal and disordered systems (see, also, Refs. 15 and 16). It should be highlighted here that at the isotope substitution in the first step the short-range part of the crystal potential is changed. On the other hand, that constituted the key question of the theoretical model of the Wannier-Mott exciton model in the disordered systems.[16] Of separate importance is the fact that the quantitative investigations of the isotope composition dependence of the Wannier-Mott exciton binding energy (E_b) could be allowed to fuller testify to the E_b dependence on the Coulomb (η^2) and Frochlich (q^2) couplings. There is emerging the unique possibility of experimental investigations into the controllable effectiveness of the exciton-phonon interaction—the problem that has existed for more than four decades.[17–22] It should be added here that there are large and important applications of the isotope mixed compounds that may be wittnessed in this field.[23]

The present paper is devoted to experimental study of the renormalization of the Wannier-Mott energy spectrum on the optical (reflection and luminescence) spectra of LiH_xD_{1-x} ($0<x<1$) mixed crystals. In particular, it will be shown that the replacement of H on D (as well as Li^6 on Li^7) increases not only the value of the forbidden gap energy E_g, but exciton Rydberg-E_b also. The quantitative investigation of the dependences $E_g \sim f(x)$ and $E_b \sim f(x)$ (where x is the isotope concentration) shows that it is nonlinear and satisfactorily described by the second degree polynom. The obtained deviation from the linearity is due primarily to the isotope disorder of the crystal lattice. The last effect confirms additionally the direct observation of the broadening of the reflection and luminescence lines in the exciton spectra of the mixed crystals. The accurate measurements of zero-phonon emission line shape of the free excitons in LiH_xD_{1-x} mixed crystals is demonstrated with increasing the value of the longitudinal-transversal splitting Δ_{LT} at the enlargement isotope mass.

Our paper is organized as follows. In Sec. II we describe the experimental technique and study samples. Section III is devoted to the exciton optical spectra as well as their energy characteristics in LiH crystals. In Sec. IV we analyze the isotope effect on the exciton binding energy and we have done a comparative study of our experimental results with the theory of an exciton embedded in disorder media. Section V deals with the isotope effect on the polariton emission in LiH_xD_{1-x} mixed crystals. Section VI presents the conclusions of the present work.

II. EXPERIMENTAL

The apparatus used in our experiments has been described in several previous publications (see, e.g., Refs. 24 and 25). For clarity, we should mention here that an immersion homemade helium cryostat was used. In view of the high hygroscopy of the investigated samples,[26] the crystal was cleaved directly in liquid or superfluid helium in the cryostat bath. This made it possible to prepare samples with a clean surface. We found no changes in the reflection and in the free-exciton luminescence[7,24] (or resonance Raman scattering[27]) spectra when a sample with such a surface was studied for periods lasting 10–15 h. The method of the crystal growth was described before many times (see, e.g., Refs. 7, 24, and 26).

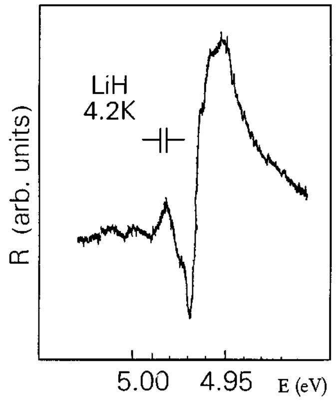

FIG. 1. Mirror reflection spectrum of LiH crystals at 4.2 K cleaved in liquid helium.

The reflection and luminescence spectra were recorded automatically. The time needed to record a spectrum did not exceed a few minutes. This made it possible to determine the spectrum at a constant temperature during spontaneous heating of the cryostat.[25] The cleaving apparatus and the cryostat construction made it possible to measure the reflection spectra in a wide range of angles of incidence.[24] The reflection spectra of the present paper were obtained at an angle of incidence of 45°. Since the degree of homogeneity of the study samples, the quality of their crystal structure, and the presence of impurities depended largely on the conditions during growth and subsequent annealing in a hydrogen (deuterium) atmosphere (see Ref. 26 and references therein), the samples selected for the investigation were those characterized by a weak topographic dependence of the reflection and luminescence spectra. The x-ray-diffraction investigation shows[28] that the LiH_xD_{1-x}-mixed crystals form a continuous row of the solid solution and are like virtual crystals with variable lattice constants which obey Vegard's law.

The UV signal was recorded by using a cooled photomultiplier and a high-sensitivity photon counting system with data storage facilities.[27] Powerful mercury and deuterium lamps were used as the light sources. The reflectance spectra of the investigated crystals[29] with a clean surface had a distinctly expressed exciton structure. However, in spite of the identical structure of all free-exciton luminescence spectra, it is necessary to note a rather big variation of the luminescence intensity of the crystals from the different batches observed in experiment.

III. RESULTS AND DISCUSSIONS: EXCITON STATES IN LiH

The specular reflection spectra of a LiH crystal with a clean surface at 4.2 K is depicted in Fig. 1. As can be seen, the spectrum possesses a well-developed structure. The long-wavelength maximum produces the energy $E=4.950$ eV and

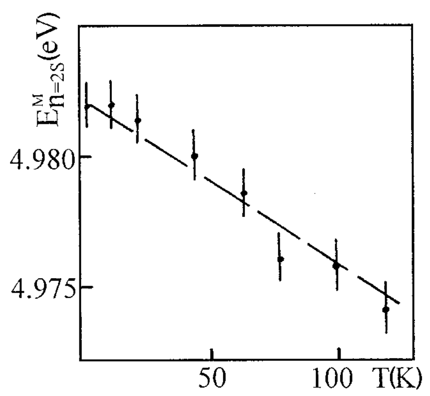

FIG. 2. Temperature shift of the second band maximum energy in the reflection spectrum which is due to the first excited state of the exciton.

which has a pronounced peculiarity at its short-wavelength side in the vicinity 4.960 eV.[27] After this result the analogous structure of this peak in the reflection spectra of crystals with a clean surface is observed in a whole series of papers (see, e.g., Refs. 30 and 31). In the short-wavelength vicinity from this band after the dispersion dip the second maximum with the energy $E=4.982$ eV is observed. Most semiconducting and insulating compounds possess such a classical dispersion shape of the fundamental spectra. With the temperature increasing, the maximum of this band is shifted to the long-wavelength side (Fig. 2) and its intensity is decreased. It became undetectable at the temperature $T=115\pm5$ K (Fig. 3). These results show that the diminishing of the second band intensity is caused by the ionization processes of the states response from this band. Taken in analogy with the results of other papers (see, e.g., Ref. 32), the energy of the ionization of these states could be crudely estimated to be $\Delta E_2=k_BT$ (where k_B is Boltzman constant). This estimation yields for this state $\Delta E_2\cong10$ meV. It should be remarked that the long-wavelength shift of this state as the temperature increases is distinguished from the speed of the shift of the long-wavelength band in the reflection spectra (for details, see Ref. 25). A large value of the reflection coefficient [0.7–0.9 (Ref. 31)], the first long-wavelength peak and relatively small half-width [$\Delta E<25$ meV (Ref. 31)], as well as sharp temperature dependence enables us to link the peaks of E_1 and E_2 with the first two members of the hydrogenlike series of the Wannier-Mott exciton. The large oscillator strength of these states indicates that the electron transition is direct[33] and is realized on the Brillouin-zone boundary at the X point. According to energy band calculation,[34,35] this corresponds to the transiton between the X_1 and X_4 points of the Brillouin zone, where the energy gap is at its minimum.

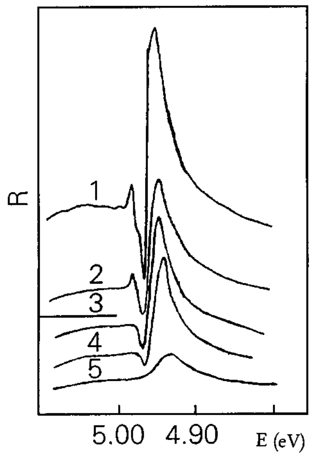

FIG. 3. Influence of temperature on the reflection spectrum of an LiH crystal T (K): (1) 2, (2) 71, (3) 138, (4) 220, and (5) 288.

The assumptions about the hydrogenlike character of the energy exciton spectrum in LiH crystals are apparently natural as far as:

(1) The observed intensity relation of the two first peaks in the reflection spectrum in accordance with the theory[36] for the allowed direct transition is close to the $\sim n^{-3}$ law, where n is the main quantum integer.

(2) The energy distance between these peaks (Δ_{12}) is substantially less than the longitudinal-optical (LO) phonon's energy ($\hbar\omega_{\mathrm{LO}}=140$ meV). The small parameter theory $E_b/\hbar\omega_{\mathrm{LO}}=0.3$ for LiH crystals. For comparison we will indicate that, for CdS, where the large radius exciton model ''works'' very well, this parameter equals 0.74 (see, e.g., Ref. 38).

(3) In benefit of the aforementioned, the application of the Wannier-Mott model to the excitons in LiH crystals could be attributed to the fact that the analogous structure as a rule consisting of two lines, is observed in the reflection spectrum of the many semiconductor compounds.[37–40]

On the strength of the above, and taking into consideration the long-wavelength peaks E_1 and E_2 energy, we obtained the next value of the exciton Rydberg for LiH crystals: $E_b=4/3\,\Delta_{12}=42$ meV (where $\Delta_{12}=E_2-E_1$ and $\Delta E_2=11$ meV). This is possible because the reflection spectra of both LiH and LiD crystals possess similar long-wavelength structure. Here ΔE_2 is the binding energy of the first excited state determined from the hydrogenlike formula

$$E_b=\mu e^4/2\hbar\varepsilon^3n^2, \tag{1}$$

where μ is the reduced exciton mass and ε,n are the dielectric permeability and the main quantum integer, respectively. The rest of the values in formula (1) are conventional. The value of $\Delta E_2=Eb/4$ is obtained with formula (1) which correlates quite well to the previous estimations of thermoionization energy of the $n=2$ exciton state. Independent determination of the exciton binding energy in these crystals is carried out also on the thermoquenching of the free-exciton luminescence intensity. Assuming that it is responsible for the ionization of the exciton ground state, the exciton binding energy of the value of 40 ± 3 meV for LiH crystals[41] was obtained.

The small energy gap between the $n=1$ and $n=2$ energy levels of the exciton state should show evidence of the strong screening effect of the Coulomb potential coupled electron and hole in the exciton. The strong screening effect of the Coulomb potential is directly indicated in the relatively large radius of the exciton state in LiH crystals and, consequently, on the small velocity of the relative motion coupling charges.[33] According to Haken,[17] in the Coulomb potential we must insert the complete value of ε_0. If there is a comparatively strong scattering of the excitons on the LO phonons (in the free-exciton luminescence[24] and resonance

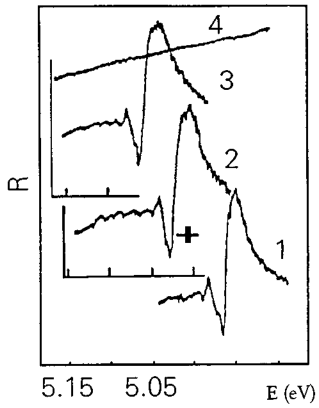

FIG. 4. Specular reflection spectra of LiH (1), $LiH_{0.4}D_{0.6}$ (2), and LiD (3) crystals with clean surface recorded at 4.2 K. Curve 4 gives the distribution of the intensity of light from a lamp source that passed through the apparatus in the absence of a crystal.

Raman[27] spectra can be observed up to five LO phonon's replicas) then there must be a drop in the $n=1$ exciton level from the Rydberg's seria. However, additional investigation shows that, in the case of LiH crystals, the situation is not the same. As far as the deviation of the $n=1$ energy level from the hydrogenlike position, it does not exceed $0.1E_b$.[33]

By knowing E_b it can be determined that the band-gap energy transitions are $E_g=E_1+E_b=4.992$ eV (at $2<T<4.2$ K). In comparison we can indicate that, in accordance with the energy band-structure calculations, the meaning of this value varies from $E_g=6.61$ eV (Ref. 34) to 5.24 eV.[35] This comparison directly indicates, on the other hand, that the agreement between theory and experiment are far from close.

IV. ISOTOPE EFFECT ON WANNIER-MOTT EXCITON LEVELS

Effect of the isotope disorder on the exciton energy spectrum

The mirror reflection spectra of pure LiD and mixed crystals cleaved in liquid helium are shown in Fig. 4. There the reflection spectra of LiH crystals with a clean surface is depicted for comparison also. All the spectra are obtained in identical conditions. As is clearly seen, the pictured spectra have the same long-wavelength structure. This is allowed to connect its nature with the excitation ground and first excited exciton states. The energy at the exciton maxima, obtained for pure and mixed crystals at 2 K is listed in Table I. The exciton binding energy E_b, deduced from a hydrogenlike expression [formula (1)], and the energy of interband transitions E_g are included in Table I also. As the deuterium concentration increases there are distinct manifestations of the three effects in the reflection spectra:

(1) The short-wavelength shift of the reflection spectrum as a whole;

(2) The different velocity of the shift of the maxima of the ground and the first excitation exciton states;

(3) Broadening of the long-wavelength maximum which is due to excitation of the ground exciton states (see, also, Ref. 31).

TABLE I. Energies at the peaks in the exciton reflection spectra recorded at 2 K for pure and mixed crystals, and also the values of E_b and E_g (all in meV).

	LiH	$LiH_{0.82}D_{0.18}$	$LiH_{0.40}D_{0.60}$	LiD
E_1	4950	4967	5003	5043
E_2	4982	5001	5039	5082
E_b	42	45	48	52
E_g	4992	5012	5051	5095

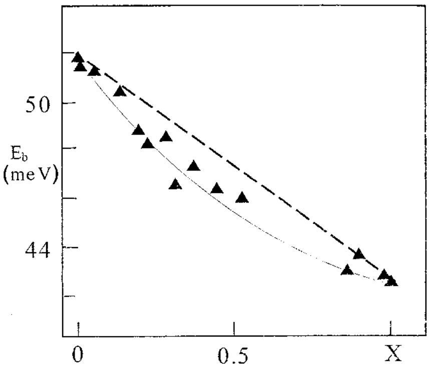

FIG. 5. The concentration dependence of exciton binding energy. The triangles are the experimental values and the continuous curve is the calculated value. The dashed line is a result of virtual-crystal model.

In accordance with the second effect (see, also, Table I), as is to be expected, there is nonlinear dependence of the exciton binding energy on the isotope concentration. This assumption is in agreement with the experimental results depicted in Fig. 5. Displayed in Fig. 5 is the Wannier-Mott exciton binding energy value which is determined by the hydrogenlike expression [Eq. (1)] using E_1 and E_2 values from the reflection spectra. The nonlinear nature of the dependence $E_b \sim f(x)$ is similar to the theoretical results,[16] where the influence of the chemical disorder of the crystal lattice on the Wannier-Mott exciton binding energy was seen and obtained a qualitative agreement with experimental results on the $GaAs_xP_{1-x}$ samples (see, Ref. 16).

Before the comparison of our experimental results with the theory developed by Elliott and Kanehisa, it would be prudent to briefly review the main properties of their theoretical model. According to Ref. 16 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

$$H=\mathbf{p}_1^2/2m_c+\mathbf{p}_2^2/2m_v+u(\mathbf{r}_1-\mathbf{r}_2)+V_c(\mathbf{r}_1)+V_v(\mathbf{r}_2), \quad (2)$$

with both the Coulomb interaction u and the potential V_ν due to disorder ($\nu=c,v$). (Reference 16 neglected disorder-induced interband mixing). As it is well known, in place of the electron-hole coordinates, ($\mathbf{r}_1$,$\mathbf{p}_1$) and ($\mathbf{r}_2$,$\mathbf{p}_2$), one may introduce the center-of-mass and relative coordinates, ($\mathbf{R}$,$\mathbf{P}$) and ($\mathbf{r}$,$\mathbf{p}$) to rewrite (1) as

$$H=\mathbf{p}^2/2m_r+u(\mathbf{r})+P^2/2M+V_c[\mathbf{R}+m_v\mathbf{r}/M]$$
$$+V_v[\mathbf{R}-m_c\mathbf{r}/M], \quad (3)$$

where m_r and M are the reduced and total masses, respectively. Because of the random potential, the translational and the relative degrees of freedom cannot be decoupled. This is essentially difficult when considering the two-body problem in a disordered system.[18] However, when the exciton state in question is well separated from other states so that the energy spacing is much larger than the translational width and disorder, one can forget about the relative motion and just apply any single-particle alloy theory (see, e.g., Ref. 18 and references therein) solely to their translational motion. For each exciton state the translational part of Hamiltonian in this case is

$$H_t = \mathbf{P}^2/2M + \overline{V_c}(\mathbf{R}) + \overline{V_v}(\mathbf{R}). \tag{4}$$

Here $\overline{V_c}$ and $\overline{V_v}$ are averages of V_c and V_v. This approach is very similar to the Born-Oppenheimer adiabatic approximation. Such situations hold in some mixed alkali halide and probably II-VI crystals. On the contrary, 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 III-V 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[18] in solving the Bethe-Salpeter equation 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 (see, also, Ref. 21). In the cited theoretical model, the average (or ''virtual crystal'') gap is given by

$$E_g^{\mathrm{vc}}(x) = E_0 + (\delta_c - \delta_v)(x - 1/2), \tag{5}$$

where E_0 is average gap, δ_c, δ_v are the values of the fluctuation broadening of the conduction and valence bands, respectively. Reference 16 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 model. It should be added here the key feature of the model developed in Ref. 16 is the short-range nature of the Coulomb potential.

At the isotope substitution changed primarily is the short-range part of the crystal potential. Therefore it is not accidental that in the experiment observed the nonlinear dependence of $E_b \sim f(x)$ describes quite well the polinom of the second degree deduced in the above cited paper:[16]

$$E_b = E_b^{\mathrm{crys}} - E_{\mathrm{bow}}[1 - W/2u_0] - E_{\mathrm{eff}}, \tag{6}$$

$$E_{\mathrm{eff}} = x(1-x)\delta_c\delta_v/W, \tag{7}$$

$$E_b^{\mathrm{crys}} = u_0 + W^2/2u_0 - W. \tag{8}$$

In expressions (6)–(8), $W = W_c + W_v$, where W_c and W_v are the width of the conduction and valence bands equal 21 eV (Ref. 42) and 6 eV,[43] respectively. Here $E_{\mathrm{bow}} = 0.046$ eV (Ref. 13) is the bow parameter obtained from the dependence of $E_g \sim f(x)$. In the calculations δ_c and δ_v equal 0.103 and -0.331 eV, respectively. E_b^{crys} is the value of the exciton binding energy in the absence of the disorder effect of the crystal lattice. As is seen from Fig. 5 the given parameter values used in Eqs. (6)–(8) make it possible to describe the nonlinear nature of the concentration dependence of the exciton binding energy quite well. From this it follows that the exciton binding energy decreasing (relative linear law—see dashed line in Fig. 5) in the vicinity of the middle meaning concentration really calls out the fluctuative 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 shallowing of the exciton levels and, respectively, the reduction of E_b. As we can see the disorder effect on the exciton level does not practically influence it. The obtained conclusion about the nature of the nonlinear dependence of the exciton binding energy on the isotope concentration is rather well accorded with the observed broadening, especially the long-wavelength maximum in the reflection spectrum (see Fig. 4). The broadening value of this band is composed from 1.5–2 at the transition from pure LiH to the pure LiD crystals. In the capacity of the dimension, the line's broadening is taken to be its half-width. It is determined in the standard manner as the spacing between the maximum and minimum in the dispersion downfall taking it on the half-height (see, also, Ref. 44). Using the results pictured in Fig. 4 and obtained on the other crystals, the concentration dependence of the halfwidth ΔE^R of the long-wavelength band in the exciton reflection spectra is reproduced in Fig. 6. In spite of a large dispersion and a limited number of used crystals it does not show the clearly followed trend of the nonlinear increase ΔE^R with diminishing x. In addition starting with $x \sim 0.5$, there is observed a saturation of the value ΔE^R. Similar dependences of the half-width line ΔE^R in the exciton reflection spectra of the solid solution semiconductor compounds II-VI and III-V are observed very often (see, e.g., Ref. 45). In the indicated paper, the observed broadening exciton lines are linked with the nonhomogeneity broadening causing the exciton interaction with a potential of a large-sized fluctuation of the solid solution composition. Efros and Raikh (see, Ref. 45 and references therein) used the method of the optimal fluctuation,

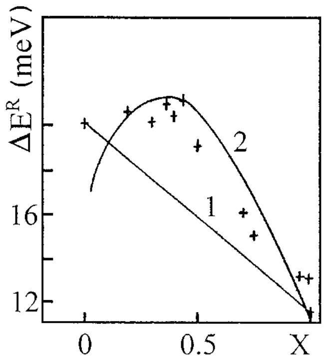

FIG. 6. The concentration dependence of the half-width line of the ground exciton state in the reflection spectra at 2 K. The full line is the calculated one using formula (9).

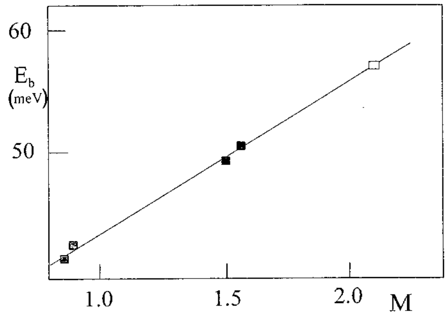

FIG. 7. The exciton binding energy dependence on the reduced mass of ions, using the next values of M (Li^6H, Li^7H, Li^6D, Li^7D, Li^7T).

where they obtained the formula of the concentration dependence of the exciton reflection lines broadening which has the expression

$$\Delta E^R = 0.5\alpha[x(1-x)/Nr_{\text{exc}}]^{1/2}. \tag{9}$$

In this formula $\alpha = dE_g/dx$ and $E_g = E_{11} + (E_1 - E_{11} - b)x + bx^2$, E_1 and E_{11} are the values of E_g for LiD and LiH, respectively and $b = 0.046$ eV is the bow parameter.[13] In expression (9) N is the site lattice concentration in which can be placed the substitution atoms, r_{exc} which is the radius of the exciton, which value varies from 47–42 Å at the transition from LiH to LiD.[31] The calculation results of formula (9) are depicted in Fig. 6 (the full line). The experimental results are placed more closely to the calculated curve than to the direct line of the virtual-crystal model. At the same time, the comparison of the experimental results with the theoretical calculations can only show qualitative agreement. Nonetheless even this qualitative analysis is a clear indicator of nonlinear dependence of the broadening value on the isotope concentration and isotope disorder, respectively. When the isotope is substituted the LO phonon energy is also changed (see, e.g., Refs. 3–5) therefore the exciton-phonon coupling (in the first step, the Frohlich one[17]) will be nonlinear depending on the isotope concentration also. In conclusion, it is worth noting that the nonlinear dependence of the free-exciton luminescence line's broadening in germanium[11] as well as lithium hydride[46] is due to the isotope disorder of the crystal lattice also.

The renormalization of the exciton binding energy at the isotope effect

At the 100% isotope substitution the exciton binding energy varies about 20% and from 42–52 meV (see, also, Table I). It is easy to see that in the frame of the virtual-crystal model the exciton binding energy in the LiT crystals will be equal to 57 meV (see Fig. 7). From this it follows that in the linear approximation the dependence of the exciton binding energy on the isotope effect may be written

$$E_b = E_b^0(1+\gamma). \tag{10}$$

Here E_b is a pure Coulomb exciton binding energy (that is in nonvibrating or frozen lattice) equals 31.5 meV in our case. The angular coefficient (see Fig. 7) equals $\beta = 12.18$ meV/M, where M is the reduced mass of lithium and hydrogen (D,T) ions and $\gamma = \beta M / E_b^0$.

Describing formula (1) for the frozen lattice (see, e.g., Ref. 21)

$$E_b^0 = \eta^2 \hbar \omega_{\text{LO}}, \tag{11}$$

we obtain for the dimensionless electron-hole coupling of the Coulomb interaction $\eta^2 = 0.47$. Comparing the values of η^2 and Frohlich exciton-phonon coupling $g^2 = 0.32$,[47] it is seen that they are very close. Thus the Frohlich and Coulomb interaction between LO phonons and electrons and holes in the exciton should be taken into account in the same manner. It became evident that the dependence E_b is taken into consideration on the isotope effect, so far as formulas (1) and (6) both do not depend on it. Really at $x = 0$, formula (6) does not work and in formula (1) ε_0 and ε_∞ are connected by the Liddane-Sachs-Teller relation and the relative change ε_∞ at the isotope substitution is rather small.[48] Since the value $\hbar\omega_{\text{LO}}$ is safely measurable for any concentration of x (see, also, Ref. 4), owing to formula (11) it can easily be reconstructed not only for the Coulomb interaction coupling η^2, but for g^2 also. It also can be seen from their relation with each other $g^2 = \eta^2(1 - \varepsilon_\infty/\varepsilon_0)$. Thus a quantitative study of the Wannier-Mott exciton binding energy simultaneously with LO phonon energy opens a unique possibility in the experimental reconstruction of the Coulomb and Frohlich couplings in the crystals with the isotope effect. The easily controlled isotope composition of the crystal is allowed, on the other hand, to create systems with variable Coulomb and Frohlich interactions that could be extremely important for the applied tasks (see, also, Ref. 41).

V. ISOTOPE EFFECT ON THE POLARITON EMISSION

Excitonic polaritons are coupled-mode excitations made up from excitons interacting with photons.[49] They represent elementary excitations propagating in crystals with frequencies in the vicinity of the fundamental edge. During the last three decades polaritons have been studied through absorption (reflection), luminescence, and light-scattering effects (see, e.g., Refs. 50–52). As is well known the dynamical properties of the excitons depend crucially on the hierarchy of couplings with the other excitations (photons, phonons, etc.[53]) In the case of dominant exciton-photon couplings it leads to excitonic polaritons, and to excitonic polarons for the dominant exciton-phonon coupling. In this way it is very interesting to study the dependence of the polariton states on the different strength of the exciton (polariton)-phonon interaction (see, also, Refs. 54 and 55). The investigation of a crystal with isotopical substitution represents a unique opportunity for this purpose. Really, for isotope substitution, the electronic structure (in the first approximation[31]) is unperturbed, but the LO phonon energy and polariton-phonon coupling should be drastically changed.

In this section we present experimental evidence of the influence of isotope substitution on the polariton emission in LiH (LiD) single crystals. With photoexcitation above the intrinsic absorption edge, luminescence of LiH (LiD) crystals is observed. The spectra of this luminescence are depicted in Fig. 8. They contain a double zero-phonon emission line and five wider LO phonon replicas. For simplicity in the

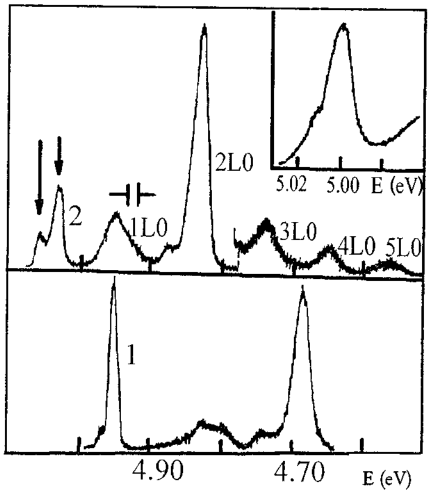

FIG. 8. Luminescence spectra of LiH (1), LiD (2) crystals cleaved in liquid-helium temperature at $T=2$ K. The inset shows the zero-phonon line of $\mathrm{LiH_{0.55}D_{0.45}}$ mixed crystals at liquid-nitrogen temperature.

case of LiH crystals only two LO phonon lines are shown ($\hbar\omega_{\mathrm{LO}}=104$ and 140 meV for LiD and LiH, respectively (see, e.g., Ref. 4)). The half-width lines of LO replicas is mainly due to the Maxwell distributions of excitons on the kinetic energy.[46] It manifests itself in a broadening of the Maxwellian shape of these lines and in redistribution of their intensity with the temperature (see, also, Ref. 56). The half-widths of the long-wavelength component of the zero-phonon line for LiH crystals at 2 K is ~13 meV. For LiD crystals this line is wider. Moreover, it is evidently seen that the zero-phonon splitting value (~25 meV) in LiD is more than in the LiH crystal ($\Delta_{\mathrm{LT}}=18$ meV, see Fig. 9). The latter value is in a rather good agreement with the splitting values obtained in reflectance[27,30] and resonant Raman-scattering experiments[27] for these crystals with a clean surface (see, also, Ref. 57).

The double structure of the zero-phonon emission line under observation could be understood proceeding from the polariton dispersion curves which, as is well known, represent a smooth conversion of the dispersion of photons in the crystals $E=\hbar c\mathbf{k}$ to a dispersive curve of excitons $E=E_0+\hbar^2\mathbf{k}^2/2M$, where $\mathbf{k}$ and M are the wave vector and the translational mass of excitons. As was shown by Toyozawa,[53] it is the region of the ''bottleneck'' that gives rise to the processes of resonant exciton absorption and the emission of light by the crystal (see, also, Ref. 49). In such a case the character of the double structure is due to the radiative decay states of the upper and lower polariton branches. (Their positions are indicated in Fig. 8 by the arrows). At elevated temperatures the maximum of the polariton energy distribution in the crystals shifts towards higher energies and the population of the upper polariton branch is enhanced. As we can see in Fig. 9 (curve 2) at $T=105$ K, it brings about a growth of the high-energy maximum of the exciton emission line with respect to the low-energy one. This result agrees very well with numerous and analogous ones cited in the literature (see Refs. 52–54). For the intermediate isotope concentration ($x=0.55$) we observed (see inset of Fig. 8) in the luminescence spectra an analogous double-structure zero-phonon emission line but its width is more than in the parent crystals (see, also, Refs. 58 and 59). At the present time it seems to us that this is the main reason for this broadening isotope disorder. But a more exact answer needs more experimental and theoretical elaborations of this task.

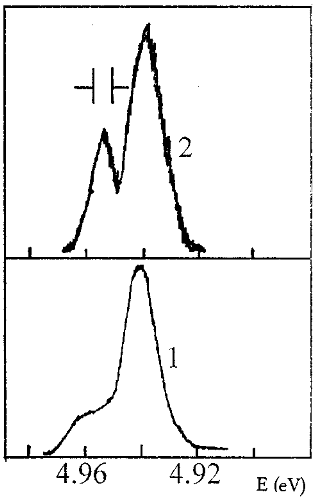

FIG. 9. Polariton emission of the LiH crystal cleaved in liquid-helium temperature at 4.2 K (1) and 105 K (2).

Returning to the results depicted in Fig. 8 and comparing the values of Δ_{LT} we can see its rise from 18 for LiH up to 25 meV for the LiD crystal. Inasmuch as the transition from LiH to LiD changes only the energy of the LO phonons,[4] we can suppose that the main reason for the renormalization of Δ_{LT} is a change of the polariton-phonon coupling. By taking into account the difference between the exciton binding energy in LiH and LiD (see, Table I) crystals and the dependence of the value Δ_{LT} on the exciton oscillator strength, we can write (see, also, Ref. 59) $\Delta_{\mathrm{LT}}=\mathscr{R}^2/E_g$. Put in this formula the value $\mathscr{R}^{(1)}=40$; $\mathscr{R}^{(2)}=50$ meV as well as $E_g^{(1)}=4.992$ eV and $E_g^{(2)}=5.095$ eV, we obtain $\Delta_{\mathrm{LT}}^{(1)}/\Delta_{\mathrm{LT}}^{(2)}=0.65$. If we consider the experimental value $\Delta_{\mathrm{LT}}^{2}=25$ meV for LiD crystals then we obtain $\Delta_{\mathrm{LT}}^{(1)}=16$ meV. The latter value is a bit less than the observed one for LiH crystals. This difference (in our estimations approximately ≅25%) may be connected with the polariton-phonon renormalization (see, also, Ref. 60). The mechanism of this renormalization is not understood yet because the acoustic-phonon branches are not altered at the isotope substitution.[61] Since the dependence of the longitudinal-optical phonon energy LO(Γ) on the isotope concentration is nonlinear,[4] we may expect the nonlinear dependence of Δ_{LT} on the isotope concentration. Thus, the accurate measurement of the zero-phonon line emission of free excitons is unambiguously witnessed about the increase of the longitudinal-transversal splitting value at the growth of the isotope's mass.

VI. CONCLUSION

In the present paper we have shown the results of the quantitative study of the isotope effect renormalization of the Wannier-Mott exciton energy spectrum. For this purpose we performed accurate measurements at the low-temperature mirror reflection and intrinsic luminescence spectra of $\mathrm{LiH}_x\mathrm{D}_{1-x}$ mixed crystals with a clean surface. As a result the nonlinear increase of the Wannier-Mott exciton binding energy E_b and interband transitions energy E_g on the growth isotope's mass has been observed. The nonlinear nature of the dependence $E_b \sim f(x)$ is quite well described by the second-order polinom on the concentration in the frame of the Wannier-Mott model in a disorder system with short-range Coulomb potential. Primarily such dependence is due to the fluctuative broadening of the valence and conduction bands with the isotope disorder. With represented experimental results the constant of the electron-hole Coulomb interaction ($\eta^2 = 0.47$) is reconstructed. The comparison of the value η^2 and the Frohlich exciton-phonon interaction constant g^2 has led to the conclusion about the necessity to take into consideration these interactions by the equivalent manner at the calculations of the isotope effect on the Wannier-Mott exciton levels. The control isotope composition is allowed to create the systems with regulated effectiveness of the exciton-phonon (exciton-photon) interaction.

The increase of the isotope's mass is responsible for the renormalization of the longitudinal-transverse splitting value. This conclusion was obtained by direct observation in the polariton emission spectra of the larger value Δ_{LT} in LiD crystals than in LiH ones. The observed increase of the Δ_{LT} value is tentatively interpreted as intensifying the polariton-phonon interaction. At the same time it is worth emphasizing that with the increase in the isotope's mass (replacement of H on D), only the optical part of the phonon spectra is changed, while the acoustic branches are not practically changed.

ACKNOWLEDGMENTS

I am grateful to Professor F. F. Gavrilov for his generous supply of samples used in these investigations and A. V. Emelyanenko for help in carrying out the experiment in the early stage of this work.

---

[1] G. Gerzberg, *Spectra of Diatomic Molecules*, Vol. 1 of *Molecular Spectra and Molecular Structure* (Van Nos Reinhold, New York, 1939), Vol. 1.

[2] J. Bauche and R.-J. Champeau, Adv. At. Mol. Phys. **12**, 38 (1976).

[3] K. C. Hass, M. A. Tamor, T. R. Anthony, and W. F. Banholzer, Phys. Rev. B **45**, 7171 (1992); J. Spitzer, P. Etchegoin, M. Cardona, T. R. Anthony, and W. F. Banholzer, Solid State Commun. **88**, 509 (1993).

[4] V. G. Plekhanov and V. A. Veltri, Sov. Phys. Solid State **33**, 2384 (1991); V. G. Plekhanov, Opt. Spectrosc. (St. Petersburg) **76**, 59 (1994); Phys. Rev. B **51**, 8874 (1995).

[5] V. F. Agekyan, V. M. Asnin, A. M. Kryukov, and I. I. Makarov, Sov. Phys. Solid State **31**, 2082 (1989); H. D. Fuchs, C. H. Grein, R. I. Devlen, J. Kuhl, and M. Cardona, Phys. Rev. B **44**, 8633 (1991); P. Etchegoin, H. D. Fuchs, J. Weber, M. Cardona, K. Itoh, and E. E. Haller, *ibid.* **48**, 12 661 (1993).

[6] A. F. Kapustinsky, L. M. Shamovsky, and K. S. Bayushkina, Acta Physicochim. (USSR) **7**, 799 (1937).

[7] V. G. Plekhanov, in *Proceedings of the 20th International Conference on the Physics of Semiconductors*, edited by E. M. Anastassakis and J. D. Joanopoules (World Scientific, Singapore, 1990), p. 1955.

[8] F. I. Kreingold, K. F. Lider, and L. E. Solovjev, JETP Lett. **23**, 679 (1976); Sov. Phys. Solid State **19**, 3158 (1977); F. I. Kreingold, *ibid.* **27**, 2839 (1995) (in Russian).

[9] F. I. Kreingold, Sov. Phys. Solid State **20**, 3138 (1978); **28**, 3164 (1986).

[10] F. I. Kreingold, K. F. Lider, and M. B. Shabaeva, Sov. Phys. Solid State **26**, 3490 (1984).

[11] G. Davies, J. Hartung, V. Ozhogin, K. Itoh, W. L. Hansen, and E. E. Haller, Semicond. Sci. Technol. **8**, 127 (1993); C. Parks, A. K. Ramdas, S. Rodriguez, K. M. Itoh, and E. E. Haller, Phys. Rev. B **49**, 14 244 (1994).

[12] A. T. Collins, S. C. Lawson, Gordon Davies, and H. Kanda, Phys. Rev. Lett. **65**, 891 (1990).

[13] V. G. Plekhanov, Solid State Commun. **76**, 51 (1990).

[14] *Optical Properties of Mixed Crystals*, edited by R. J. Elliott and I. P. Ipatova (North-Holland, Amsterdam, 1988).

[15] W. Schafer and J. Treusch, Solid State Commun. **43**, 949 (1982).

[16] V. A. Kanehisa and R. J. Elliott, Phys. Rev. B **35**, 2228 (1987).

[17] H. Haken, *Quantum Field Theory of Solids* (North-Holland, Amsterdam, 1976).

[18] S. D. Mahanti and C. M. Varma, Phys. Rev. B **6**, 2209 (1972); S. D. Mahanti, *ibid.* **10**, 1384 (1974).

[19] J. Sak, Phys. Rev. B **6**, 2226 (1972).

[20] V. Fedosejev, Phys. Status Solidi B **59**, 715 (1973).

[21] A. A. Klochikhin, Sov. Phys. Solid State **22**, 1690 (1980).

[22] Jai Singh, in *Solid State Physics: Advances in Research and Applications*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1984), Vol. 38, p. 295.

[23] E. E. Haller, J. Appl. Phys. **77**, 2857 (1995).

[24] V. G. Plekhanov, A. V. Emelyanenko, and A. U. Grinfelds, Phys. Lett. A **101**, 291 (1984).

[25] V. G. Plekhanov, Phys. Solid State (St. Petersburg) **35**, 1493 (1993).

[26] G. I. Pilipenko, A. Abirzyanov, D. V. Oparin, and F. F. Gavrilov, J. Phys. Condens. Matter **4**, 4055 (1992).

[27] V. G. Plekhanov and V. I. Altukhov, J. Raman Spectrosc. **16**, 358 (1985).

[28] W. B. Zimmerman, Phys. Rev. B **5**, 704 (1972).

[29] At room temperature and ordinary pressure LiH forms a cubic crystal lattice (NaCl-like), e.g., consisting of two cubic-centered lattices displaced one relative to another on one half of the lattice constant. The compounds with such crystal structure belong to the O_h^5 space group. Comparing the ion radius $r_{\mathrm{Li}^+} = 0.68$ Å and $r_{\mathrm{H}^-} = 1.5$ Å and the lattice constant size $a = 2.042$ Å, it is seen that in LiH crystals the Li and H ions are significantly overlapped. The melting temperature of the LiH (LiD) crystals equals 961 (964) K.

[30] R. A. Kink, M. F. Kink, and T. A. Soovik, Nucl. Instrum. Methods Phys. Res. Sect. A **261**, 138 (1987).

[31] V. G. Plekhanov, Opt. Spectrosc. (St. Petersburg) **79**, 778 (1995).

[32] B. Segall and D. T. F. Marple, in *Physics and Chemistry of II-VI Compounds*, edited by M. Aven and J. Prener (North-Holland, Amsterdam, 1967), Chaps. 1 and 7.

[33] V. G. Plekhanov, T. A. Betenekova, and V. A. Pustovarov, Fiz.

Tverd. Tela **18**, 2438 (1976) [Sov. Phys. Solid State **18**, 1422 (1976)].

[34] A. B. Kunz and D. J. Mikish, Phys. Rev. B **11**, 1700 (1974).

[35] S. Baroni, G. Pastori Parravicini, and G. Pezzica, Phys. Rev. B **32**, 4077 (1985).

[36] R. J. Elliott, Phys. Rev. **108**, 1384 (1957).

[37] B. Segall and G. D. Mahan, Phys. Rev. **171**, 935 (1968).

[38] S. A. Permogorov, in *A11BV1 Physics* (Science, Moscow, 1986), p. 146 (in Russian).

[39] V. F. Agekyan, Phys. Status Solidi A **43**, 11 (1977).

[40] *Excitons*, edited by M. Sturge and E. I. Rashba (North-Holland, Amsterdam, 1982).

[41] V. G. Plekhanov, Opt. Spectrosc. (Leningrad) **69**, 822 (1990).

[42] J. Kama and N. Kawakami, Phys. Lett. A 126, 348 (1988).

[43] T. A. Betenekova, I. M. Shabanova, V. A. Trapesnikov, and F. F. Gavrilov, Fiz. Tverd. Tela (Leningrad) 20, 1426 (1978) [Sov. Phys. Solid State **20**, 820 (1978)].

[44] N. N. Ablyazov, A. G. Areshkin, V. G. Melekhin, L. G. Suslina, and D. L. Fedorov, Phys. Status Solidi B **135**, 217 (1986).

[45] A. L. Efros and M. E. Raikh, in *Optical Properties of Mixed Crystals* (Ref. 14), Chap. 8.

[46] V. G. Plekhanov and A. V. Emelyanenko, Fiz. Tverd. Tela (Leningrad) **34**, 1705 (1992) [Sov. Phys. Solid State **34**, 906 (1992)].

[47] V. G. Plekhanov and V. I. Altukhov, Fiz. Tverd Tela **23**, 774 (1981) [Sov. Phys. Solid State **23**, 439 (1981)].

[48] J. L. Anderson, J. Nasise, K. Philipson, and E. Pretzel, J. Phys. Chem. Solids. **31**, 613 (1970).

[49] S. I. Pekar, *Crystal Optics and Additional Light Waves* (Benjamin Cummings, Menlo Park, NJ, 1983).

[50] E. Koteles, in *Excitons* (Ref. 40), Chap. 2.

[51] C. Weibuch and R. G. Ulbrich, in *Light Scattering in Solids*, edited by M. Cardona and G. Guntherodt (Springer, Berlin, 1982), p. 111.

[52] M. S. Brodin, E. N. Myasnikov, and S. V. Marisova, *Polaritons in Crystal Optics* (Naukova Dumka, Kiev, 1984) (in Russian).

[53] Y. Toyozawa, Progr. Theor. Phys. (Kyoto) Suppl. **12**, 111 (1959).

[54] A. L. Ivanov and L. V. Keldysh, J. Exp. Theor. Phys. **84**, 404 (1983) (in Russian).

[55] A. L. Ivanov, J. Exp. Theor. Phys. **90**, 158 (1986).

[56] E. F. Gross, *Selected Papers* (Science, Leningrad, 1976) (in Russian).

[57] V. G. Plekhanov, Phys. Solid State (St. Petersburg) **36**, 3177 (1994).

[58] H. Mariette, Y. Marfaing, and J. Camassel, *Proceedings of the 18th International Conference on the Physics of Semiconductors* (World Scientific, Singapore, 1987), Vol. 11, p. 1409.

[59] R. S. Knox, *Theory of Excitons* (Academic, New York, 1966).

[60] V. G. Plekhanov, Phys. Lett. A **203**, 242 (1995).

[61] J. L. Verble, J. L. Warren, and J. L. Yarnell, Phys. Rev. **168**, 980 (1968).