0.1 Experimental Evidence Of The Strong Phonon Scattering In Isotopical Disordered Systems: The Case LiH$_x$D$_{1-x}$.

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Abstract. We present Raman spectra of LiH$_x$D$_{1-x}$ mixed crystals at room temperature and in a wide range of isotope compositions (0 < x < 1). The line broadening and energy shift of the Raman lines for the optical phonons were investigated for the first time. The observation of the local mode vibration, the two-mode behaviour of the LO (Γ) phonons at large isotope concentration as well as large lines broadening directly evidence the strong additional phonon scattering due to the isotope-induced disorder. The obtained results could not describe in the weak phonon scattering approximation of the CPA model.

Some of the most interesting and important effects in the atomic vibrations of solids arise from the presence of small concentration of impurity (defects) in the perfect lattice. The important effects of the point defects are the following. Firstly, the addition of a small impurity content may destroy the translational symmetry of the unperturbed perfect crystal in addition to slight change of its lattice modes. Such changes are often sufficient to allow interaction with light radiation in cases where it would not occur otherwise (absorption process etc.). Secondly, the impurity atoms often introduce special modes into the phonon spectrum which are not characteristic for the host lattice as a whole but rather that for the atomic environment surrounding the impurity. These special vibrational modes are called local modes, gap modes and resonant band modes (see, e.g. [1,2]). As it is well-known, a localised mode is characterized by its high frequency which lies above the maximum vibrational frequency of the perfect host crystal. The amplitude of this vibration is very large at the impurity site and decreases ASH very rapidly with increasing distance from the impurity. A gap mode has a frequency which lies in the gap between the optical and acoustic bands. If the impurity content of a solid is increased to such an extent that interaction between impurity atoms begins to play an effective role, the systems should then be named a disordered solid rather than an impure crystal.

The case is of particular interest when the impurity atoms are of the same chemical nature, but have a different mass, i.e., the case of isotopic impurities. In this case no deformation of the unit cells at the substitutional sites occurs, and, since the crystal potential remains the same as in the isotopically pure material, only the vibrational kinetic energy is affected by the mass impurities. As it is well-known [1,2] the lattice phonons in an atomic (ionic) crystal are true collective motions of the atoms. The impurity atoms are involved in the
collective motion, but, owing to their different mass, they will follow the motion with a different amplitude, thus giving rise to a change in the phase of the motion. The impurities therefore play the role of scattering centers for the phonons and their effect then can be described in terms of scattering processes. In the case of optical phonons this will lead to a shift and to a broadening of the phonon band in the Raman scattering spectra.

The effect of isotope substitution and its influence on the LiH lattice dynamics has a long history. IR-absorption and reflection [3-5], neutron scattering [6] as well as Raman scattering [7-13] studies allow us to discover the local [7] and gap [3] modes in the vibration spectra of LiH-D mixed system. According to these studies the energy of the LO phonons at the Γ point of the Brillouin zone is equal to 840 and 1100 cm\(^{-1}\) for LiD and LiH and for the local (LiD-H) and gap (LiH-D) modes - respectively 917 and 580 cm\(^{-1}\). Moreover, the first paper [14] dealing with the fundamental absorption, spectra of thin films of LiH and LiD showed that the longwavelength (actually, exciton) peak of LiH is shifted towards shortwavelength relative to that of LiD. This shift is 0.65 meV [14] at room and 103 meV [15] at liquid helium temperature.

In recent years the effects of the isotopic substitution and disorder on the phonon states of germanium [16,17] and diamond [18,19] have attracted considerable interest, triggered by the availability of nearly isotopically pure materials. There, it was shown that the results obtained on the shift and broadening of the phonon lines could be accurately described at the limit of the weak phonon scattering of the phonon coherent potential approximation (CPA) model [20,21]. In the limit of weak phonon scattering the small parameter of the theory is \(\Delta M/M < 1\) (where \(\Delta M\) is mass difference between the various isotopes and \(M\) is average isotope mass), and the scattering potential due to the mass defects is not strong enough to localize the Γ point LO phonons.

In case of LiH-D mixed system the parameter \(\Delta\mu/\mu^*/\mu\) \(1/2\) (where \(\mu\) is the reduced effective mass of the unit cell) is not small. Therefore for this system we may expect to be at the other extreme case, in which the scattering potential is quite strong. In this letter we report the first results on the effects of the anharmonicity and isotopic disorder on the vibronic properties of Li\(_{1-x}\)D\(_x\) \((0 < x < 1)\) mixed crystals, first of all concerning the optical phonons. The optical method selected for investigation is the classical Raman - scattering technique. In particular, not only will the two-mode behaviour of the LO(Γ) phonons at the large concentration \((x \equiv 0.5)\) be shown, but also the direct connection of the shift and broadening of their lines with a large anharmonicity as well as a strong phonon scattering due to the isotopically induced disorder. Additionally, our experimental results are direct evidence of the transition from local mode vibration to the LO (Γ) phonons. The experimentally observed asymmetry of the optical phonon lines is due to isotope-induced disorder as well.

The apparatus used in the present study has been described elsewhere (Ref. 13 and 22 and the references cited therein). For convenience, however, we shall briefly mention the principal points. Crystals were excited by various argon laser lines (particularly 514.5, 488.0 and 467.5 nm) and also by the second harmonic line of a YAG-Nd\(^{3+}\) laser \((\lambda_L = 532\) nm). In all these cases the laser
power was between 50 and 200 mW, depending on the intensity of the scattered line which varied by more than one order of magnitude. The Raman spectra were obtained using an automatic apparatus based on a double-grating monochromator. The signal from this monochromator was recorded with a cooled photomultiplier operating as a photon counter. The results are stored in the memory of a personal computer, used also to control the apparatus. The counting time usually did not exceed 10 s. A typical slit width was less than 150 µm. To suppress plasma fluorescence an appropriate interference spike filter was used in the incident beam. The 90° scattering geometry was used most frequently, but similar results were obtained also in backscattering configuration. Both LiH and mixed crystals based on it were highly hygroscopic. Therefore, special measurements were performed to monitor the state of the surface of our samples. Most convenient method was to follow the peak in the Raman spectra at $1450 \text{ cm}^{-1}$, which represented the molecular vibrations of $\text{CO}_2$ [23] or a peak at $w = 500 \text{ cm}^{-1}$ due to $\text{OH}$ vibrations [4,5]. Our samples were thick plates freshly cleaved from high-quality bulk single crystals grown by a modification of the Bridgman-Stockbarger methods (see [24,12,15] and the literature cited therein). Apart from chemical and mass-spectroscopical isotope concentration [12,24] their composition was verified also from the energetic nomogram of the exciton ground state extracted from low temperature reflectance and luminescence spectra. The last one is possible as far as the exciton ground state reconstruction in the whole concentration interval ($0 < x < 1$) possesses the one-mode character (for details see Ref. 25).

Fig. 1. Second-order Raman spectra of $\text{LiH}_x\text{D}_{1-x}$ mixed crystals: $x = 0$ (1); $0.05$ (2); $0.12$ (3) and $0.35$ (4).

Fig. 1 shows a family of the Raman spectra of $\text{LiH}_x\text{D}_{1-x}$ mixed crystals with relatively low hydrogen concentration ($x < 35\%$). Analogous spectra of the mixed crystals with a large isotope concentration is depicted on the Fig. 2.

Fig. 2. Second-order Raman spectra of $\text{LiH}_x\text{D}_{1-x}$ mixed crystals: $x = 0$ (1); $0.42$ (2); $0.76$ (3) and $1.0$ (4). The arrows indicated the transition from LO(Γ) phonon and local mode peaks of $\text{LiD}$ crystal to LO(Γ) phonon peak of $\text{LiH}$ crystal via an intermediate LO peaks of $\text{LiH}_x\text{D}_{1-x}$ mixed crystals.

First of all it is important to remark here on the close agreement between the pictured spectra of virgin LiH and LiD and previously published data [7-13]. Moreover, the practically constant low frequency structure of all the spectra is remarkable, primarily associated with lithium ion vibrations [9 -13,22]. The exception was the lowest frequency peak whose intensity decreased on the increase in $x$ and its origin is connected with the substraction of the tranverse optical and acoustical phonons. As it was shown previously [22], the practically linear nature of this dependence could be used, in addition to other methods [25], as, an independent means for determining the composition of $\text{LiH}_x\text{D}_{1-x}$ mixed crystals. On the other hand, the high frequency part of the Raman spectra connected with excitation of the optical phonons, changes considerably with the increase in $x$.  

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Although from the exciton states nomogram \[25\] it can be concluded that the investigated crystal (Fig. 1, curve 1) is pure LiD, a high frequency peak can be clearly observed in the spectral region \(\simeq 1850 \text{ cm}^{-1}\) (it is more significant at the excitation with \(\lambda_L = 532 \text{ nm}\) (see, also [13]). It must be mentioned that such a peak has not been observed in pure LiH crystals. This peak has been observed before in the second-order Raman spectra of LiD crystals and attributed, as mentioned above, to the local vibration of hydrogen \[7\]. The peak observed in our spectra at \(\simeq 1850 \text{ cm}^{-1}\) corresponds to \(2\omega_{\text{loc}}\). Although the actual concentration of H in the used LiD crystal is very low and unknown, it can certainly be accounted for the observed local mode in the second-order Raman spectra. As we see, the increasing concentration causes the growth in the local mode band intensity and a small shift of the frequency. This behaviour remains up to \(x < 10\%\) (for details see Ref. 10). These results are in close agreement with the calculated concentration dependence of the intensity and \(\omega_{\text{loc}}\) of the local vibration (see, also Ref. 20,21). With a further increase of \(x\) according to the results on the low temperature exciton luminescence and resonant Raman spectra [15] the system consists of mixed crystals. We should emphasize here that the successive investigation of the isotope concentration dependence of the local vibration line’s shape allows us to measure the percolation threshold of these mixed crystals (for details see, also Ref. 20,26 and references therein).

Returning to Fig. 2 in detail we examine the analysis of the Raman spectra structure of LiH\(_x\)D\(_{1-x}\) mixed crystals at the large isotope concentration. With the further increase \(x > 0.15\) we observed the decrease of the 2LO (\(\Gamma\)) phonon maximum intensity of the virgin LiD crystal with a simultaneous growth of the higher frequency peak intensity of the LiH\(_x\)D\(_{1-x}\) mixed crystals. The last one was attributed also to the renormalized LO (\(\Gamma\)) vibrations in the mixed crystals (see, also Ref. 22). The final limit of this peak is the position of LO (\(\Gamma\)) phonon peak of the virgin LiH crystal (Fig. 3).

Fig. 3. Isotope composition dependence of the (a) linewidth (FWHM) and (b) frequency of the optical phonons in the Raman spectra of LiH\(_x\)D\(_{1-x}\) mixed crystals: a) 1, \(\lambda_{\text{excit}} = 253.7 \text{ nm}\); 2 - \(\lambda_L = 488.0 \text{ nm}\). b) 1 - results the present paper; 2, results on the IR-absorption TO(\(\Gamma\)) phonons in thin film of LiH-D mixed system [3].

As mentioned above the LiH\(_x\)D\(_{1-x}\) mixed crystals at small \(x\) value must have a two-mode character reconstruction of the optical phonons. Moreover, according to the results of ref. 20 the observable situation with the optical phonon rearrangement in LiH\(_x\)D\(_{1-x}\) crystals satisfies also the analytical criterion of the two-mode reconstruction at small isotope concentration: \(1/2W < \delta < W\). Here \(\delta\) and \(W\) are the frequency shift of TO (\(\Gamma\)) phonon caused by the isotopical defect and the band width of optical vibrations respectively [27]. In Ref. 20 it is also noted that it is necessary to fulfil the more rigid condition \(\delta > W\) to maintain the two-mode behaviour of the phonon spectra up to an isotope concentration \(x \simeq 0.5\).
The last result is obtained in a very crude approximation. Indeed, in Ref. 20 a model phonon spectrum was used for the calculation consisting of two Gaussian bands and limited by $\omega_{TO} < \omega < \omega_{LO}$. Nevertheless it is necessary to note, that this approximation does not greatly influence on the relation between $W$, and $\delta, \varepsilon_0, \varepsilon_\infty$, because the values used in Ref. 20 were real (see, also Refs. 22,27). In Fig. 3 we plotted the results from Fig. 1,2 as well as the data obtained for other crystals. From Fig. 3b it is seen that two-mode optical phonons behavior is observed up to $x < 0.4$. The comparison of the optical phonon band width $(W)$ with the maximal shift $(\delta)$ of the transverse optical phonon frequency at the change of $H$ to $D$ shows [22] that the condition $W > \delta$ is always fulfilled (see, also Ref. 27). That relation contradicts the phonon CPA model prediction about two-mode optical phonons rearrangement at $x \approx 0.5$. In our opinion this discrepancy is due primarily to the strong isotope-induced additional phonon scattering because the potential changes considerably on isotopic substitution in LiH crystals. The observation of the local mode vibration at small $x$ (see Fig. 1) may serve as further support for this conclusion. This conclusion agree with the results of ref. 17. where it was emphasized that the observation of the local mode vibration directly evidences the strong potential changes at the isotope substitution. Therefore the weak phonon scattering approximation in the CPA model is insufficient for the description of our experimental results. On the other hand, the obtained conclusion quite agrees with the fact that the parameter $\Delta \mu / \mu$ is not small for LiH-D system. As it is well-known for Ge and C, the parameter $\Delta M / M$ at the isotopically substitution is extremely small (e.g. $<< 1$) and the weak phonon scattering approximation of the CPA model is sufficient to describe the experimental results in Refs. 17-19.

Now we are going to discuss briefly the dependence of the broadening LO phonon lines on the isotope concentration (Fig.3a). The measured Raman linewidth (see, also Fig. 4) is larger near the center of the composition range than near the end points. it should be added that the width of the LO phonon line depends not only on isotope concentration but also on the excitation energy.

Fig.4. Line shape of the excited light (1), 2LO line scattering at 4.2 K in LiH (2) and LiH$_x$D$_{1-x}$ mixed crystals ($\lambda_{excit} = 253.7$ nm).

The results shown in Fig. 4 are the same as those obtained in earlier paper [27] using uncoherent ultraviolet ($\lambda_{excit} = 253.7$ nm) radiation for the excitation of the crystals. The observable addition structure on the shortwavelength side of the 2LO ($\Gamma$) phonon replicas line in the Raman spectra is due to the resonant excitation of the 2LO ($L$) phonons (for details see Ref. 27 and references therein). Although the results depicted in Fig. 3a are very similar to the results on diamond [18] it is necessary to remark on the strong difference between our results on the two-mode behavior of the LO($\Gamma$) phonons (at $x < 0.4$) and one-mode LO($\Gamma$) phonons in diamond. This difference, as well as the observation of the local mode vibration (at small $x$) in the LiH$_x$D$_{1-x}$ crystals, unambiguously allows us to make conclude about the strong potential changes on the
isotope substitution. Probably the nonlinear dependence of the frequency shift and broadening LO phonon lines in the Raman spectra on $x$ may reflect the nonlinear character of the unharmonicity [29].

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Figure captions

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27. Here $W$ is the zone width, that is a difference between LO and TO phonons and has the following expression: $W = \omega_{TO} (\epsilon_0 - \epsilon_\infty) / (\epsilon_0 + \epsilon_\infty)$, where $\epsilon_0$ and $\epsilon_\infty$ have the conventional meaning are equal to $\epsilon_0 = 12.9$ and $14.0$ and $\epsilon_\infty = 3.61$ and $3.63$ for LiH and LiD respectively.
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