Fundamentals and Applications of Isotope Effect in Modern Technology

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Different crystals (semiconductors and insulators) with varying isotopic composition have been recently grown. I discuss here the effect of isotopic mass and isotopic disorder on the properties (vibrational, elastic, thermal and optical) of different crystals. The main applications of the stable isotopes are included self-diffusion, neutron transmutative doping (NTD) of different semiconductors, optical fibers, isotope-based quantum computers, etc. Because of space limitations this discussion will not exhaustive. I hope however, to give sufficient references to published work so that the interest reader can easily find the primary literature sources to this rapidly expanding field of solid state physics.

KEYWORDS: phonons, excitons, isotope-mixed crystals, laser materials, isotope-based quantum computers

I. Introduction

It is well-known that the presence of randomly distributed impurities in a crystal can give rise to significant variations of its mechanical, electrical, thermal, and optical properties with respect to those of the pure solid. All these properties are, more or less, directly related to the structure of the manifold of phonon states and any variation induced in this structure by the presence of the impurities, will produce a corresponding alteration of the physical properties of the material. Of particular interest is the case in which the impurity species is of the same chemical nature, but with a different mass, i.e. the case of isotopic impurities. The mechanisms by which the impurities (isotopes) perturb the phonon distribution will depend on the mass difference between the host and guest species.1–3 Phonons are the crystal excitations most directly related to the isotopic masses. In monatomic crystals (like C, Ge, Si, etc.), and within the harmonic approximation, all phonon frequencies scale like the square root of the average isotopic mass. Namely, this feature can be used for the nondestructive isotopic characterization investigated materials. The isotopic effect can be classified into two categories: 1) The first type is caused by the variation of the phonon frequencies with the average isotopic mass. To this type belongs the isotopic effect in superconductors, which plays an important role in the search for the mechanism of high Tc superconductivity (see, e.g. Ref. 4)). The effect of changing the atomic mass M is to change the phonon frequencies ω according to:

\[ \omega = \sqrt{\omega/M}, \]

where \( \omega \) is a force constant characteristic of the phonon under consideration. The change in atomic mass implies, at low temperatures (see below), a change in the average atomic displacement for each phonon mode. In the case of one atom per primitive cell the mean squared phonon amplitude \( \langle u^2 \rangle \) is given by:1,2

\[ \langle u^2 \rangle = \frac{\hbar^2}{(4M\omega)}[1 + 2n_B(\omega)] \]

where \( n_B(\omega) \) is the Bose-Einstein statistical factor, \( \omega \) is the frequency of a given phonon and \( \langle \ldots \rangle \) represents an average over all phonon modes. The average in r.h.s. of Eq. (2) is often simplified by taking the value inside \( \langle \ldots \rangle \) at an average frequency \( \omega_D \) which usually turns out to be close to the Debye frequency. We should distinguish between the low temperature (\( \hbar\omega > k_BT \)) and the high temperature (\( \hbar\omega < k_BT \)) limits and see:

\[ \langle \hbar\omega > k_BT \rangle, \quad \langle u^2 \rangle = \left( \frac{\hbar}{4M\omega_D} \right) \sim M^{1/2} \]

independent of \( T \) and

\[ \langle \hbar\omega < k_BT \rangle, \quad \langle u^2 \rangle = \left( \frac{k_BT}{2M\omega^2} \right) \sim T \]

independent of \( M \).

Using Eq. (1) we can find from last equations that \( \langle u^2 \rangle \), the zero-point vibrational amplitude, is proportional to \( M^{-1/2} \) at low temperatures: it thus decrease with increasing \( M \) and vanishes for \( M \rightarrow \infty \). For high \( T \), however, we find that \( \langle u^2 \rangle \) is independent of \( M \) and linear in \( T \) ((for details see Ref. 3) and references therein).

Another type of isotope effects is produced by the isotopic mass fluctuations about the average mass \( \langle M \rangle \). These fluctuations perturb the translational invariance of a crystal and lift, at least in part, \( k \)-vector conservation. The most striking effect of this type is observed in the thermal conductivity which has a maximum at a temperature \( T_D \) (see for example Ref. 5)). The concentration of the impurity \( ^{13}\text{C} \) from the standard 1% (against 99% of \(^{12}\text{C} \)) by a factor of ten increases the thermal conductivity of diamond by about a factor of two, a fact that leads to amplifications in situations where a large amount of generated heat has to be driven away (e.g. as substrates for high power electronic devices (see Ref. 5)). As is well-known this maximum represents the transition from boundary scattering to the phonon umklapp scattering regime and its value \( \kappa_m \)
II. Results and Discussion

The coordinate of the center of the scattering line is proportional to the square root of the reduced mass of the unit cell, i.e. \( M^{-1/2} \). It is precisely this dependence that is expected in the harmonic approximation (for details see Ref. 3). An additional frequency shift of the line is observed for the natural and enriched germanium specimens and is equal, as shown in Refs. 7 and 9) to 0.34±0.04 and 1.06±0.04 cm\(^{-1}\), respectively (see also Fig. 7 in Chap. 4 of Ref. 10)). Detailed calculation of the shape of the lines in RS of semiconductors have been performed by Spitzer et al.\(^{11}\) In their paper a quantitative agreement with the experimental data on diamond and germanium has been obtained. Comparing the half-widths of the scattering lines in first-order RS in diamond and germanium (see Fig. 1), it is easy to see that the observed line broadening due to isotopic disorder in diamond is much greater than that in germanium. The reason for this is that the \( k=0 \) point is not the highest point in the diamond dispersion curve (see Fig. 10b in Ref. 7), whereas in the case of germanium it is the highest point.\(^{12}\) This shift of the maximum from the \( \Gamma \)-point \((k=0)\) leads to a much larger density of states in the vicinity of \( \omega_{\text{LTO}} \) in comparison with the normal one calculated by the formula:

\[
N_L \sim \text{Re}(\omega_{\text{LTO}} - \omega + i[\Delta \omega_{\text{LTO}}/2])^{1/2}
\]  

(for more details see Ref. 12)). The density of states in diamond is asymmetric with respect to \( \omega_{\text{LTO}} \) causing asymmetry in the shape of the scattering line.\(^{13}\) This asymmetry also leads to the asymmetric concentration dependence of the half-width of the scattering line. As was shown early (see, e.g. Ref. 3) and references therein), in the case of a weak potential of isotopic scattering of phonons, their self-energy \( \hat{\epsilon}(\omega) \) does not depend on \( q \) (-phonon quasiimpuls). This is precisely the situation observed for C and Ge. Indeed, if we express the mass fluctuation \( \Delta M/M \) (\( M \) is the mean mass of all isotopes) in the form of the variation of the phonon band width \( \Delta \omega_0=12\text{ cm}^{-1} \) at \( q=0 \) and compare it with the width of the band of optical phonons in Ge equals to \( \approx 100\text{ cm}^{-1} \), we will see that the variations very small. Under this conditions the localization of optical phonons in Ge is naturally, absent, and as observed in experiment, they stay delocalized (see below, however opposite case in LiH, D\(_{1-}\)-crystals). Moreover, direct measurements of the phonon lifetime in Ge show that, in the case of anharmonic decay, it is two orders of magnitude shorter than the lifetime that is due to the additional scattering by isotopes, i.e. \( \tau_{\text{anharm}} = \tau_{\text{disord}} \cdot 10^{-2} \).\(^{13}\) Therefore, the contribution of anharmonicity to the half-width of the first-order light scattering line in Ge is two orders of magnitude greater than that caused by the isotopic disorder in crystal lattice. In conclusion of this part of our report we should mention that analogous structure of first-order RS and their dependence on isotope composition has by now been observed many times, not only in elementary Si and \( \alpha \)-Sn, but also in compound CuCl, CuBr, ZnSe, GaN semiconductors (for details see Ref. 3)).

In Fig. 2 (curve 1) the spectrum of second-order RS of light in pure LiD crystal is shown (see Ref. 7)). In spite of the fact, according to the nomogram of exciton states,\(^{14}\) the crystal studied should be considered to be pure, its RS
spectrum contains a clear high-frequency peak around 1,850 cm\(^{-1}\). The observed peak does not have an analogue in RS of pure LiH (Fig. 2, curve 4) and has already been observed earlier in the second-order RS and has been interpreted (see Ref. 7) and references therein) as a local vibration of the hydrogen in LiD crystals. Further we note that as the concentration grows further (\(x\approx0.15\)) one observes in the spectra a decreasing intensity in the maximum of 2LO(\(\Gamma\)) phonons in LiD crystal with a simultaneous growth in intensity range of 1,850 cm\(^{-1}\). The observed peak does not have an analogue in RS spectra on the short-side of the 2LO(\(\Gamma\)) peak (see Fig. 21 in Ref. 7)).

Comparison of the structure of RS spectra (curves 1 and 2 in Fig. 2) allows us, therefore, to conclude that in the concentration range of 0.1 \(\sim\)0.45 the RS spectra simultaneously contain peaks of the LO(\(\Gamma\)) phonon of pure LiD and the LO(\(\Gamma\)) phonon of the mixed LiH, D\(_{1-x}\) crystal. Thus, the second-order RS spectra of LiH, D\(_{1-x}\) crystals have one- and two-mode character for LO(\(\Gamma\)) phonons, and also contain a contribution from the local excitation at small values of \(x\). Moreover, we should add that an additional structure in RS spectra on the short-side of the 2LO(\(\Gamma\)) peak (see Fig. 21 in Ref. 7)) was observed relatively ago in mixed LiH, D\(_{1-x}\) crystals and, very recently, in isotopically mixed crystals of diamond, germanium and \(\alpha\)-Sn (for details see Refs. 3) and 11)). These effects caused by isotopic disorder in the crystal lattice of isotopically mixed crystals.\(^{3}\) The observation of two-mode behavior of the LO(\(\Gamma\)) phonons in RS spectra of LiH, D\(_{1-x}\) crystals contradicts the prediction of the CPA\(^{15}\) according to which the width W of optical vibration band should be smaller than the frequency shift (\(\Delta\)) of transverse optical phonon. However, as was shown early (see, e.g. Ref. 7) and references therein) in LiH, D\(_{1-x}\) mixed crystals, the reverse inequality is valid, \(i.e.\ W\sim|\Delta|\). According to Ref. 16), this discrepancy between experimental results and theory based on CPA\(^{15}\) is mainly explained by the strong potential of scattering of phonons, caused by a large change in the mass upon substitution of deuterium for hydrogen. One more reason of the discrepancy between theory and results of the experiment may be connected with not taking into account in theory the change of the force-constant at the isotope substitution of the smaller in size D by H ion. We should stress once more that among the various possible isotope substitution, by far the most important in vibrational spectroscopy is the substitution of hydrogen by deuterium. As is well-known, in the limit of the Born-Oppenheimer approximation the force-constant calculated at the minimum of the total energy depends upon the electronic structure and not upon the mass of the atoms. It is usually assumed that the theoretical values of the phonon frequencies depend upon the force-constants determined at the minimum of the adiabatic potential energy surface. This leads to a theoretical ratio \(\omega(H)/\omega(D)\) of the phonon frequencies that always exceed the experimental data. Very often anharmonicity has been proposed to be responsible for lower value of this ratio. In isotope effect two different species of the same atom will have different vibrational frequencies only because of the difference in isotopic masses. The ratio \(p\) of the optical phonon frequencies for LiH and LiD crystals is given in harmonic approximation by:

\[
p = \frac{\omega(H)}{\omega(D)} = \sqrt{\left[\frac{M(LiD)}{M(LiH)}\right]} \cong \sqrt{2}
\]

while the experimental value (which includes anharmonic effects) is in the range 1.396\(\sim\)1.288 (see Table 1 and

![Graph](image)

**Fig. 2** Second-order Raman spectra of LiH, D\(_{1-x}\) crystals at room temperature: 1, 2, 3 and 4; \(x\approx0, 0.42, 0.76\) and 1, respectively (after Ref. 7)).

| Table 1 | Values of the coefficients \(d\omega/dM\) (meV, cm\(^{-1}\)) for the optical phonons and the experimental and theoretical values of \(p\) as well as deviation \(\delta\%\) of these values from theoretical ones |
|----------|-----------------|----------------|
| Substances | Frequencies | \(p_{exp}\) | \(p_{theory}\) | \(\delta\%\) |
| LiH/LiD | 140 (meV)/104 (meV)\(^{124}\) | 1.288–1.344 | \(\sqrt{2}=1.414\) | 4.8–8.9 |
| SiH\(_4\)/SiD\(_4\) | 2,186.87/1,563.3 (cm\(^{-1}\))\(^{10}\) | 1.39 | \(\sqrt{2}=1.41\) | 1.5 |
| \(^{12}\)C/\(^{13}\)C | 1,332.5/1,280 (cm\(^{-1}\))\(^{10,22}\) | 1.04 | 1.041 | 0.001 |
| \(^{70}\)Ge/\(^{76}\)Ge | 309.8/297.7 (cm\(^{-1}\))\(^{10,26,27}\) | 1.041 | 1.042 | 0.096 |
| \(^{28}\)Si/\(^{30}\)Si | 524.8/509.8 (cm\(^{-1}\))\(^{28}\) | 1.029 | 1.035 | 0.58 |
| \(^{64}\)Zn/\(^{68}\)Zn | 213.2/207.4 (cm\(^{-1}\))\(^{10}\) | 1.028 | 1.029 | 0.097 |
| \(\alpha\)-\(^{124}\)Sn/\(\alpha\)-\(^{124}\)Sn | 206.5/196.8 (cm\(^{-1}\))\(^{10,30}\) | 1.049 | 1.052 | 0.30 |
| Ga/\(^{14}\)N/\(^{15}\)N | 535/518 (cm\(^{-1}\))\(^{10,31}\) | 1.033 | 1.035 | 0.19 |
| \(^{65}\)Cu/\(^{67}\)Cu | 174.4/171.6 (cm\(^{-1}\))\(^{10,32}\) | 1.016 | 1.022 | 0.59 |

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already been observed for insulators (Fig. 4) and lowest (in-isotope concentration) was found for different bound excitons in semiconductors. 20,21) The 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).15) 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 (see, e.g. Fig. 2 of Ref. 18)). Using the least-squares method was found the empirical dependence of \( E_B \) on \( \delta M \) which is presented on Fig. 5. As can be seen the mentioned dependence has a parabolic character:

\[
\ln(\delta%) = -7.5 + 2 \ln([\delta\omega] / (\partial M)). \tag{7}
\]

From the results of Fig. 3, it can be concluded that only hydrogen compounds (and its isotope analog-deuterium) need to take into account the force-constant changes in isotope effect. It is also seen that for semiconductor compounds (on Fig. 3-points, which is below of Ox line) the isotope effect has only the changes of the isotope mass (for details see Refs. 3 and 7).

The dependence of the band gap energy on isotopic composition \( (\text{via mechanism of electron-phonon interaction}) \) has already been observed for insulators \( (\text{Fig. 4}) \) and lowest (indirect-direct) gap of different semiconductors \( (\text{and references therein}) \). It has been shown to result primarily from the effect of the average isotopic mass on the electron-photon interaction, with a smaller contribution from the change in lattice constant. Reference 19) was the first paper where the exciton binding energy \( E_B \) was found to depend on the isotopic composition. It was shown further that this change in \( E_B \) was attributed to the exciton-phonon interaction (originally with LO phonons) (see, also Ref. 3)). At present time such dependence of \( E_B \sim f(x) \) (x-isotope concentration) was found for different bound excitons in semiconductors.\(^{20,21}\)

Fig. 3 The dependence of \( \ln(\delta%) \sim f(\ln([\delta\omega] / (\partial M))) \): points are experimental values and continuous line-calculation on the formula (7)

Fig. 4 Mirror reflection spectra of crystals: LiH, curve 1; LiD, curve 2 and LiD, curve 3 at 4.2 K; light source without crystals, curve 4 (after Ref. 18))

Ref. 17). In this table there are the experimental and theoretical values of \( p \) according to formula (6), as well as the deviation \( \delta = \left[(p_{\text{theory}} - p_{\text{exp}}) / p_{\text{theory}}\right] \) of these values from theoretical ones. Using the least squares method was found the empirical formula of \( \ln(\delta%) \sim f(\ln([\delta\omega] / (\partial M))) \) which is depicted on Fig. 3. As can be seen the indicated dependence has in the first approximation a linear character:

\[
\ln(\delta%) = -7.5 + 2 \ln([\delta\omega] / (\partial M)). \tag{7}
\]

From the results of Fig. 3, it can be concluded that only hydrogen compounds (and its isotope analog-deuterium) need to take into account the force-constant changes in isotopic effect. It is also seen that for semiconductor compounds (on Fig. 3-points, which is below of Ox line) the isotope effect has only the changes of the isotope mass (for details see Refs. 3 and 7).

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\[
\ln(\partial E_g) / (\partial M) = 6.105(E_g)^2 - 7.870(\ln E_g) + 0.565. \tag{8}
\]

From this figure it can be concluded also that the small variation of the nuclear mass \( (\text{as in semiconductors}) \) causes the small changes in \( E_g \) also. When the nuclear mass increases it causes the large changes in \( E_g \) (C, LiH, CsH, etc.) (for details, see Ref. 18)).

Detailed analysis the process of self-diffusion in isotope pure materials and hetero-structures was done in Ref. 5). Interest in diffusion in solids is as old as metallurgy or ceramics, but the scientific study of the phenomenon may probably be dated some sixth-seven decades ago. As is well-known, the measured diffusion coefficients depends on the chemistry and structure of the sample on which it is measured. In cited paper\(^{5} \) it was shown to use the stable isotopes for the study of diffusion process in different semiconducting structures (bulk, hetero-structures etc.).

Chapter 6 of the book\(^{5} \) describes the new reactor technology-neutron transmutative doping (NTD). Capture of ther-
nal neutrons by isotope nuclei followed by nuclear decay produces new elements, resulting in a large number of possibilities for isotope selective doping of solids. The importance of NTD technology for studies of the semiconductor doping as well as metal-insulator transitions and neutral impurity scattering process is underlined. The low-temperature mobility of free carriers in semiconductors is mainly determined by ionized- and neutral-impurity scattering. The ionized-impurity scattering mechanism has been extensively studied (see e.g. Ref. 5) and references therein), and various aspects of this process are now quite well understood. Scattering by neutral impurities is much less than by ionized centers, i.e., its contribution is significant only in crystals with low compensation and at very low temperatures where most of the free carriers are frozen on the impurity sites. The availability of highly enriched isotopes of Ge which can be purified to residual dopant levels $<10^{12}$ cm$^{-3}$ has provided the first opportunity to measure neutral impurity scattering over a wide temperature range. In paper$^{20}$ three Ge isotopes transmute into shallow acceptors (Ga), shallow donors (As) and double donors (Se) (see also above):

$$74^2\text{Ge} + n \rightarrow 71^2\text{Ge} \pm (r/2=11.2 \text{d}) \rightarrow 71^2\text{Ga} + \nu_e$$

$$74^2\text{Ge} + n \rightarrow 75^2\text{Ge} \pm (r/2=82.2 \text{min}) \rightarrow 75^2\text{As} + \beta^- + \nu_e,$$

$$76^2\text{Ge} + n \rightarrow 77^2\text{Ge} \pm (r/2=11.3 \text{h})$$

$$\rightarrow \beta^- + \nu_e + \frac{77^2\text{As} + \beta^- (r/2=38.8 \text{h})}{75^2\text{Se} + \beta^- + \nu_e}. \quad (9)$$

The isotopes $72^2\text{Ge}$ and $73^2\text{Ge}$ are transmuted into the stable $73^2\text{Ge}$ and $74^2\text{Ge}$ respectively. Controlling the ratio of $70^2\text{Ge}$ and $74^2\text{Ge}$ in bulk Ge crystals allows fine tuning of the majority—i.e., as well as the minority carrier concentration. Currently, this is the best method to vary the free-carrier concentration independently from compensation ratio. As opposed to other doping methods, NTD yields a very homogeneous, perfectly random distribution of the dopants down to the atomic levels.$^{51}$ Thus isotopically controlled crystals offer a unique possibility to study systematically the scattering mechanism of the charge carriers in semiconductors. Extensive Hall-effect and resistivity measurements from room temperature down to 4.2 K yielded very accurate free-carrier concentrations and mobilities as a function of temperature and doping level were done in paper.$^{51}$ Itoh et al.$^{22}$ have performed temperature-dependent Hall measurements on four different $p$-type and two different $n$-type Ge crystals (Fig. 6). Figure 6 shows the relative strength of the scattering from the ionized and the neutral impurities. There is only a relatively small temperature region in which the scattering from the neutral impurities dominates. This range extends to higher temperatures as the free-carrier concentration is increased. The calculated “transition temperatures” above which the ionized impurities are the main scattering centres compare very well with experimental results of Itoh et al.$^{22}$ (see also Fig. 6.31 in Ref. 5). In order to demonstrate the importance of the homogeneous dopant distribution, Itoh et al. have performed the same study on samples cut from Ge:Ga crystals grown by the conventional Czochralski method, where Ga impurities were introduced to Ge melt during the crystal growth. These authors observed deviations of the measured mobility from the theoretical calculations, which are most likely due to inhomogeneous Ga impurity distributions in melt-doped Ge. Only the use of NTD semiconductors with randomly distributed dopants allows for an accurate test of the neutral impurity-scattering models (for details, see Ref. 5)).

Another application of isotope pure and isotope mixed crystals that will be discussed here is related to the possibility of using an isotopically mixed medium (e.g. LiH$_i$D$_{1-x}$ or $^{13}\text{C}_i^{12}\text{C}_{1-x}$) as an oscillator of coherent radiation in the ultraviolet spectral range. To achieve this, the use of indirect electron transitions involving, say, LO phonons was planned.$^{23}$ The detection of LO phonon replicas of free-exciton luminescence in wide-gap insulators attracted considerable attention to these crystals (see e.g. Refs. 10) and 23)). At the same time it is allowed one to pose a question about the possibility of obtaining stimulated emission in UV (VUV) region (4–6 eV) of the spectrum, where no solid state sources for coherent radiation exist yet. In the first place this is related to the emitters working on the transitions of the intrinsic electronic excitation (exciton). The last one provides the high energetic yield of the coherent emission per unit volume of the substance.

In this part we will discuss the investigation results of the influence of the excitation light density on the resonant secondary emission spectra of the free-exciton in the wide-gap insulator LiH$_i$D$_{1-x}$ (LiH$_i$D$_{1-x}$ F$_x$) crystals. The cubic LiH crystals are typical wide-gap ionic insulator with $E_g = 4.992$ eV$^{10}$ with relatively weak exciton–phonon interaction however: $E_R/h\omega_{LO}=0.29$ where $E_R$ and $h\omega_{LO}$ are exciton binding energy and longitudinal optical phonon’s energy, re-
sion energy in the \(\text{LiH}_x \text{D}_{1-x} \) \((\text{LiH}_1 \rightarrow \text{F}_1; \text{LiD}_{1-x} \text{F}_x)\) mixed crystals as well as in the range 5.35–5.10 eV in \(^{12}\text{C}_x \text{C}_{1-x}\) mixed crystals (see also Ref. 10).

## III. Conclusion

In this review I have presented briefly the results of experimental and theoretical studies of the objects of research that earlier were simply inaccessible. The use of such objects (isotope controlled samples) allows the investigation of not only the isotope effects in lattice dynamics (elastic, thermal and vibrational properties) but also the influence of such effects on the electronic states \textit{via} electron–phonon interaction. The main applications of the stable isotopes are included self-diffusion (crystals, glasses, superstructures etc.), NTD of different semiconductors, optical fibers, isotope-based quantum computers etc.

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**Fig. 7** The dependence of the intensity in the maximum (1) and on the long-wavelength side (2) of 2LO replica emission line of LiH crystals on the excitation light intensity.

In insert: luminescence spectra of free excitons in LiH crystals in the region of the emission lines of 1LO and 2LO phonon repetitions at 4.2 K for low (1) and high (2) density of excitations of 4.99 eV photons (after Ref. 23).
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