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Raman spectroscopy of solids as a tool for study of phonons and defects

The goal of this work is to study physical basics and possibilities of the Raman spectroscopy as a powerful tool for the investigation of materials.

Theoretical basics

Raman scattering is an inelastic scattering of light. To understand a physical origin of this phenomenon, let us first consider an approach based on the classical electrodynamics.

Consider an infinite medium with a dielectric susceptibility χ. In the general case, dielectric susceptibility is a tensor of the second rank, but for simplicity we assume that χ is a scalar. Assume that a plane electromagnetic wave

$$\vec{F}\left(\vec{r},t\right) = \vec{F}_i\left(\vec{k}_i,\omega_i\right)\cos\left(\vec{k}_i\vec{r} - \omega_i t\right). \tag{1}$$

propagates in the medium, where $\vec{k}_i$ and ω_i are the wave-vector and angular frequency of the wave, respectively.

The incident electromagnetic wave will lead to polarization of the medium. Arising dipole moment per unit volume will be described by the relation

$$\vec{P}\left(\vec{r},t\right) = \vec{P}\left(\vec{k}_i,\omega_i\right)\cos\left(\vec{k}_i\vec{r} - \omega_i t\right), \tag{2}$$

where

$$\vec{P}\left(\vec{k}_i,\omega_i\right) = \varepsilon_0\chi\left(\vec{k}_i,\omega_i\right)\vec{F}\left(\vec{k}_i,\omega_i\right), \tag{3}$$

and ε_0 is electric constant.

If the medium is at a finite (non-zero) temperature, atomic oscillations will influence on the dielectric susceptibility, giving rise to fluctuations therein.

Как известно, смещения атомов $\vec{Q}\left(\vec{r},t\right)$, соответствующие фононам с волновым вектором $\vec{q}$ и частотой ω_0, могут быть представлены в виде плоских волн As is known, atomic displacements corresponding to phonons with a wavevector $\vec{q}$ and a frequency ω_0 may be presented in the form of plane waves:

$$\vec{Q}\left(\vec{r},t\right) = \vec{Q}_0\left(\vec{q},\omega_0\right)\cos\left(\vec{q}\vec{r} - \omega_0 t\right). \tag{4}$$

Since the amplitude of of the atomic oscillations are small compared with the lattice parameter, χ can be expanded in a Taylor series:

$$\chi\left(\vec{k}_i,\omega_i,\vec{Q}\right) = \chi_0\left(\vec{k}_i,\omega_i\right) + \left(\frac{\partial\chi}{\partial\vec{Q}}\right)_0\vec{Q}\left(\vec{r},t\right) + \dots \tag{5}$$

where χ_0 is dielectric susceptibility of the medium in which the fluctuations are absent.

Substituting (5) into (3), we can express the dipole moment:

$$\vec{P}\left(\vec{r},t,\vec{Q}\right) = \vec{P}_0\left(\vec{r},t\right) + \vec{P}_{ind}\left(\vec{r},t,\vec{Q}\right), \tag{6}$$

where

$$\vec{P}_0\left(\vec{r},t\right) = \varepsilon_0\chi_0\left(\vec{k}_i,\omega_i\right)\vec{F}_i\left(\vec{k}_i,\omega_i\right)\cos\left(\vec{k}_i\vec{r}-\omega_i t\right). \tag{7}$$

represents a dipole moment vibrating in phase with the incident radiation, and

$$\vec{P}_{ind}\left(\vec{r},t,\vec{Q}\right) = \varepsilon_0\left(\frac{\partial\chi}{\partial\vec{Q}}\right)_0\vec{Q}\left(\vec{r},t\right)\vec{F}_i\left(\vec{k}_i,\omega_i\right)\cos\left(\vec{k}_i\vec{r}-\omega_i t\right). \tag{8}$$

is polarization wave induced by vibrating atoms (phonons) or other fluctuations, as example, magnons. Substituting equation (4) to (8), we obtain:

$$\vec{P}_{ind}\left(\vec{r},t,\vec{Q}\right) = \varepsilon_0\left(\frac{\partial\chi}{\partial\vec{Q}}\right)_0\vec{Q}_0\left(\vec{q},\omega_0\right)\cos\left(\vec{q}\vec{r}-\omega_0 t\right)\vec{F}_i\left(\vec{k}_i,\omega_i\right)\cos\left(\vec{k}_i\vec{r}-\omega_i t\right) =$$
$$= \frac{1}{2}\varepsilon_0\left(\frac{\partial\chi}{\partial\vec{Q}}\right)_0\vec{Q}_0\left(\vec{q},\omega_0\right)\vec{F}_i\left(\vec{k}_i,\omega_i\right)\times\left[\cos\left(\left(\vec{k}_i+\vec{q}\right)\vec{r}-\left(\omega_i+\omega_0\right)t\right)+\cos\left(\left(\vec{k}_i-\vec{q}\right)\vec{r}-\left(\omega_i-\omega_0\right)t\right)\right] \tag{9}$$

Thus, an additional component of the dipole moment induced by the atomic vibrations, is the sum of two waves, one of which is shifted to the Stokes side (has a frequency $\omega_i-\omega_0$ and a wavevector $\vec{k}_i-\vec{q}$), and the other – to the anti-Stokes side (has a frequency $\omega_i+\omega_0$ and a wavevector $\vec{k}_i+\vec{q}$) relative to the frequency of the incident wave. It is known from electrodynamics that the dipole moment oscillating at a certain frequency emits electromagnetic waves of the same frequency. Thus, the oscillations of the dielectric susceptibility with a frequency ω_0 will lead to the appearance of two additional waves with frequencies shifted by ω_0 relative to the incident wave frequency ω_i.

The difference between the frequencies of the incident and inelastically scattered waves in Raman spectroscopy is called a Raman shift. However, most often one understand under the Raman shift k_R the difference between the wave numbers of the incident and inelastically scattered waves:

$$k_R = \frac{1}{\lambda_i} - \frac{1}{\lambda_s}, \tag{10}$$

where λ_i and λ_s are wavelengths of the incident and scattered radiation, respectively. If we multiply (10) by the product of Planck's constant h and the speed of light c, we find that the Raman shift k_R is proportional to the change of a photon energy as a result of scattering:

$$hck_R = \frac{hc}{\lambda_i} - \frac{hc}{\lambda_s} = E_i - E_s. \tag{11}$$

Substitution of the numerical values of the constants gives

$$E_i - E_s \; meV \; = 0.124 k_R \; cm^{-1} \; . \tag{12}$$

From the point of view of quantum physics of a solid state, the considered inelastic light scattering is the scattering of a photon by a phonon. Naturally, such a process must satisfy the energy conservation law. In the case of the Stokes process, a photon spends part of its energy on the creation of phonon that leads to a decrease in the light frequency. In the case of the anti-Stokes process, a phonon is absorbed by a photon resulting in an increase of its energy and, accordingly, the radiation frequency. It is obvious that the relative probability of the anti-Stokes process increases with temperature.

Expansion (5) can be extended to terms of higher orders. The terms of the second order will result in an appearance in the scattered radiation spectrum of the waves with frequencies equal to $\pm\omega_{0a} \pm \omega_{0b}$, where $\omega_{0a} > \omega_{0b}$ are frequencies of phonons involved in the process. The peaks corresponding to the Raman shifts $\omega_{0a} + \omega_{0b}$ и $\omega_{0a} - \omega_{0b}$ are called the sum and difference, respectively. If two phonons involved in the scattering are identical, the corresponding two-phonon peak is called an overtone.

In the scattering of a photon by a phonon, the momentum conservation law must also be met. This is illustrated in Fig. 1, where the wavevectors of the incident $\mathbf{k}_i$ and scattered $\mathbf{k}_s$ photons, as well as wavevectors $\mathbf{q}$ of phonon participating in the scattering are shown (for definiteness, the Stokes process is considered). When the crystal is illuminated with the visible range light, the wavelength is about three orders of magnitude larger than the lattice parameter. Accordingly, the photon wave vector is three orders of magnitude smaller than the first Brillouin zone. Therefore, in the one-phonon scattering only phonons at the center of the Brillouin zone can participate. With regard to the multiphonon scattering, the momentum conservation law means that the sum of the wavevectors of the phonons involved in the process must be equal to zero. In this case, the wave vector of each of these phonons can take any value within the Brillouin zone.
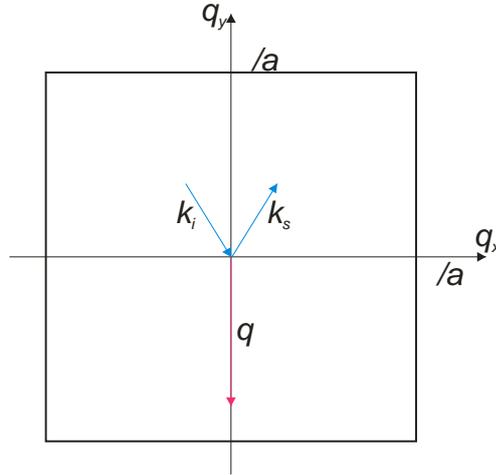

Fig. 1 – The momentum conservation law for a one-phonon scattering

We calculate the possible number of one-phonon lines in the Raman spectrum of the crystal. If the unit cell contains s atoms, it has $3s$ freedom degrees. Three of them characterize the position in space of the cell as a whole, the three branches of acoustic vibrations correspond to them. It is known that the frequencies of the acoustic oscillations at $q = 0$ become zero, therefore in the scattering by acoustic phonons with q close to zero the photon energy does not change (the Raman shift is zero). The remaining $3s-3$ freedom degrees characterize the arrangement of atoms in a cell relative to each other; $3s-3$ branches of the optical vibrations

correspond to them. In this case, however, the number of one-phonon lines generally will not equal to 3s–3. Firstly, not all vibrations are active in the Raman spectra. Indeed, if this or that oscillation does not change the dielectric susceptibility of the crystal, the corresponding phonons does not appear in the Raman spectra. Secondly, for polar vibrations (i.e. for vibrations leading to change of the cell dipole moment) the frequencies of the longitudinal (LO) and transverse (TO) phonons are different (LO – TO splitting). Third, the same frequency may correspond to different variations (degenerated oscillations). Thus, we can draw a conclusion: lower symmetry of the lattice leads to more lines corresponding to one-phonon scattering in Raman spectra, and vice versa. For example, for the diamond-type lattice the Raman spectra contain only one one-phonon line.

Since each material is characterized by its unique set of vibrational branches (and, consequently, the set of frequencies of optical phonons with $q = 0$), the measurement of the Raman spectra can serve as an effective method of the phase analysis.

Let us obtain an expression for the intensity of inelastically scattered radiation. It is known from electrodynamics that the radiation intensity depends on the polarization of the scattered light as $\left| \vec{P}_{ind} \vec{e}_s \right|^2$, where $\vec{e}_s$ is the polarization vector of the scattered wave. Using relation (9), we find that the intensity of the scattered radiation I_s is proportional

$$I \propto \left| \vec{e}_i \left(\frac{\partial \chi}{\partial \vec{Q}} \right)_0 \vec{Q} \; \omega_0 \; \vec{e}_s \right|^2 , \tag{13}$$

where $\vec{e}_i$ is the polarization vector of the incident wave. Because $\vec{Q}$ is the displacement vector of the atom, $\dfrac{\partial \chi}{\partial \vec{Q}}$ is a third-rank tensor. If we introduce an unit vector $\hat{Q} = \vec{Q} / Q$, we can define the second rank tensor as follows:

$$R = \left(\frac{\partial \chi}{\partial \vec{Q}} \right)_0 \hat{Q} \; \omega_0 \; . \tag{14}$$

This allows to rewrite (13) in the form

$$I \propto \left| \vec{e}_i \cdot R \cdot \vec{e}_s \right|^2 . \tag{15}$$

Tensor R defined by (14) is called the Raman tensor. Raman tensors for the different types of oscillations in different types of crystal lattices are calculated using the group theory; they are reference values.

It follows from (15) that the intensity of the Raman radiation depends on the direction of polarization of the incident and scattered waves. Therefore, at the fixed directions of $\vec{e}_i$ and $\vec{e}_s$ vectors, the Raman intensity of radiation depends on the spatial orientation of the crystallographic axes of the investigated object. Thus, the Raman spectroscopy in some cases can act as a method of studying the texture of the investigated object.

We have considered above the Raman scattering in condensed matter as photon scattering by phonon. At first glance, it may seem that the electrons do not participate in this process, so it can be described mathematically by the Hamiltonian of the photon-phonon interaction. However, the intensity of this interaction will not vanishingly small only in the case when the frequencies of the photons and phonons are comparable in magnitude. In reality, however, frequency of photons used in the experiment exceed the phonon frequency more than an order of magnitude (photon energy of visible light is a few eV, whereas phonon energy is equal to tens of meV).

Interaction between photons and phonons occurs through the mediation of electrons. Scattering occurs as a result of three stages:

1. Absorption of a photon with energy $\hbar\omega_i$ by electron and its excitation.

2. The interaction of the excited electron with phonon with energy $\hbar\omega_0$ (emission in the case of Stokes scattering and absorption in the case of anti-Stokes one).

3. Transition of electron into the initial state with emission of a quantum of energy $\hbar(\omega_i - \omega_0)$ or $\hbar(\omega_i + \omega_0)$ in the case of the Stokes and anti-Stokes processes, respectively.

Thus, despite the fact that the state of the electronic subsystem is not changed as a result of inelastic scattering of a photon by a phonon, electrons are integral part of this process.

It follows from the above scheme of Raman scattering that its probability increases if the energy of the incident or the scattered photon matches any allowed electronic transitions in the system. In this case we speak of the incoming or outcoming resonances, respectively, and scattering itself is called as a resonance. Therefore, the signal intensity in the Raman spectrum depends on the electron spectrum of the investigated object. Moreover, the probability of the Raman scattering process enhances with electron-phonon interaction increasing.

So we have established what factors determine the position and intensity of the lines in the Raman spectra. Another fundamental parameter characterizing the spectral line is its width. Let us analyze the mechanisms of line broadening in Raman spectra. According to the Heisenberg uncertainty principle, there is a relationship between the lifetime of the system and the uncertainty of its energy:

$$\Delta t \cdot \Delta E \geq \hbar, \tag{16}$$

where Δt is generally lifetime of the system, and ΔE is uncertainty in the energy of this system.

With regard to the process of Raman scattering, Δt is the phonon lifetime. Phonon lifetime is determined by two fundamental processes: (i) its conversion into two others (this process is also called the phonon decay) and (ii) scattering by defects. Phonon decay processes determine the so-called natural width of the Raman line Γ_{nat}, which is approximately equal to

$$\Gamma_{nat} \approx \omega_0 \sqrt{\frac{m}{M}}, \tag{17}$$

where ω_0 is phonon frequency, m is mass of the electron, M is mass of the atom. Natural line width is related to the phonon mean free path r as follows:

$$\Gamma_{nat} \approx \omega_0 \left(\frac{a}{r}\right)^2, \tag{18}$$

where a is lattice parameter. Estimation of the natural width of the Raman line leads to values equal to several inverse centimeters.

If the defects acting as phonon scattering centers are in the material, the mean free path of the phonons will be reduced compared to the defect-free material in accordance with the relation

$$\frac{1}{r} = \frac{1}{r_{dec}} + \frac{1}{r_{def}}, \tag{19}$$

where r_{dec} is phonon mean free path in the absence of defects, r_{def} is phonon mean free path, if there were no decay processes. Thus, *the width of the Raman line is a measure of material defectsness.*

It is accepted in spectroscopy to use as a parameter characterizing the width of the spectral line its full width at half maximum (FWHM). It is obvious that FWHM as well as the position of the line can be determined "by sight". However, a better approach is to approximate the experimental spectral line shape using one or another curve. It is known from the general physics that if the line width is due to the finite lifetime of the system, the contour of the spectral line is described by the Lorenz curve

$$I\left(k\right) = I_0 \frac{\Gamma^2}{4\pi^2 \left(k - k_0\right)^2 + \Gamma^2}, \tag{20}$$

where k_0 is maximum position, I_0 is line intensity at the maximum, and Γ parameter determines the spectral width of line. It is easy to verify that FWHM is related to the value of Γ parameter by relation

$$FWHM = \frac{\Gamma}{\pi}. \tag{21}$$

Fitting the experimental spectrum by function (20), one find the parameters k_0, Γ and I_0, at which the maximum coincidence between the experimental and theoretical contours is reached. Just these k_0, Γ and I_0 values are used as characteristics of the spectral line.

As a rule, the experimental contour of Raman line is well described by the Lorenz curve. The exception is when the excited system represents a set of subsystems, between parameters of which there is a certain random scatter. If the effect of this factor on the shape of the spectral line is dominant, the contour is described by the Gaussian function and not the Lorentz function.

Example 1: Raman active phonons in the wurtzite structure

The crystal structure of wurtzite (many semiconductors, for example, ZnO have this structure) is shown in Fig. 2. The unit cell contains two atoms of each kind (Zn and O). Thus, the number of freedom degrees the cell equals 4 x 3 = 12, 3 of which correspond to the position of the cell in the space as a whole, and the remaining 9 correspond to the location of atoms relative to each other. These nine optical oscillations are shown schematically in Fig. 3. Three of them (Fig. 3, top row) correspond to the motion of atoms along the six-fold axis (direction c in Fig. 2) and are non-degenerate. Another three vibration modes (Fig. 3, bottom row) are doubly degenerate: frequencies of the atomic oscillations in two mutually perpendicular directions in the plane perpendicular to the six-fold axis are the same. Oscillations labeled as B_1(low) and B_1(high) does not lead to a change in the dielectric susceptibility of the crystal and hence фку inactive in Raman spectra. For each of two polar oscillations LO − TO splitting takes place, whereby there are six different frequencies corresponding to A_1(LO), A_1(TO), E_1(LO), E_1(TO), E_2(low) and E_2(high) phonons.
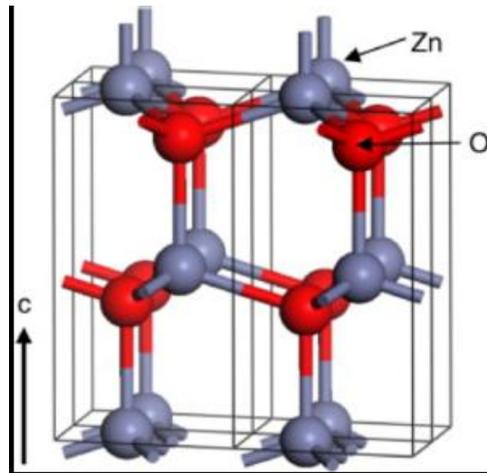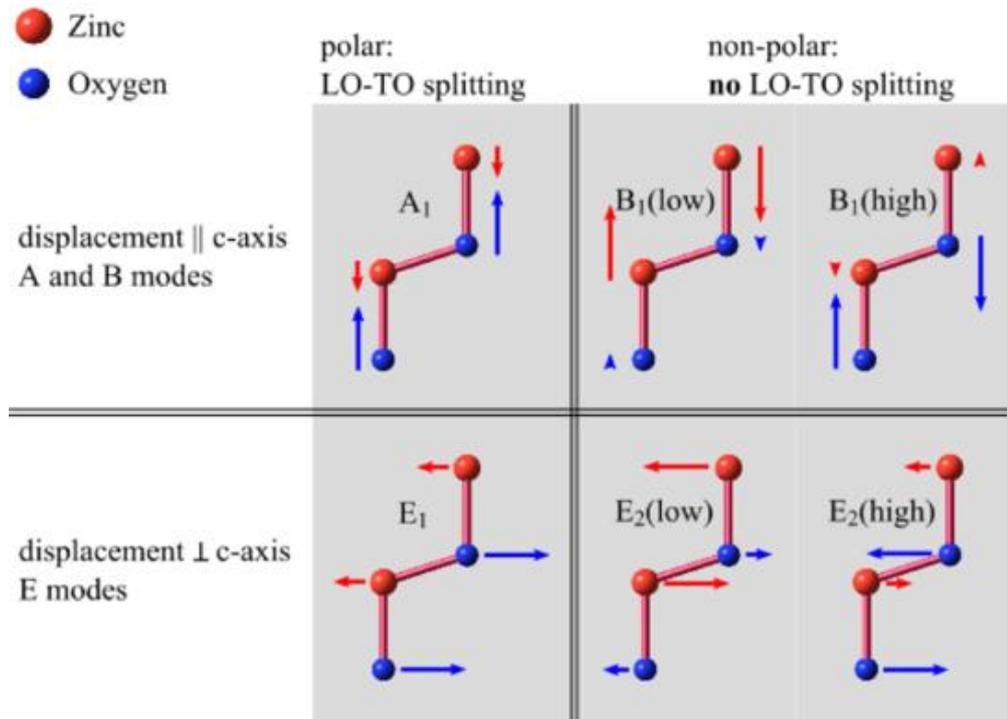
Fig. 2 – Wurtzite type crystal structure

Fig. 3 – Possible atomic oscillations in wurtzite cell

We also consider as an example the dependence of the signal intensity on the polarization of the incident and scattered waves for vibrations of A_1 symmetry. In a coordinate system where the z-axis is parallel to the sixfold axis, the Raman tensor corresponding to this oscillation has the form

$$R = \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix}. \tag{22}$$

Assume that the wave vectors of the incident and scattered waves are parallel to the sixfold axis, and the polarization vectors of these waves have the same direction. In this case, the intensity of the scattered light, according to (15), is given by the relation

$$I \square \left| \begin{bmatrix} 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix} \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \right|^2 = a^2 . \qquad (23)$$

If the polarization vectors of the incident and scattered waves are mutually perpendicular, the scattered light intensity is zero:

$$I \square \left| \begin{bmatrix} 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix} \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} \right|^2 = 0 . \qquad (24)$$

This example shows how knowing the Raman tensor of this or that oscillation to establish the intensity of the corresponding line in the spectrum depending on the polarization of the incident and scattered waves.

Determination of elastic strains. It is known that the potential of interatomic interaction has a form similar to that shown in Fig. 4. From the above dependence it is seen that the interaction strength increases in absolute value with decrease of interatomic distance. Consequently, under compression of the lattice the vibration frequencies of atoms increase, whereas under tension reduce compared with their "normal" values. Этот эффект может приводить к сдвигу положения рамановских линий порядка нескольких обратных сантиметров и может быть зафиксирован с помощью рамановской спектроскопии. This effect may lead to a shift in the position of the Raman lines by a few inverse centimeters and can be easily detected using Raman spectroscopy.
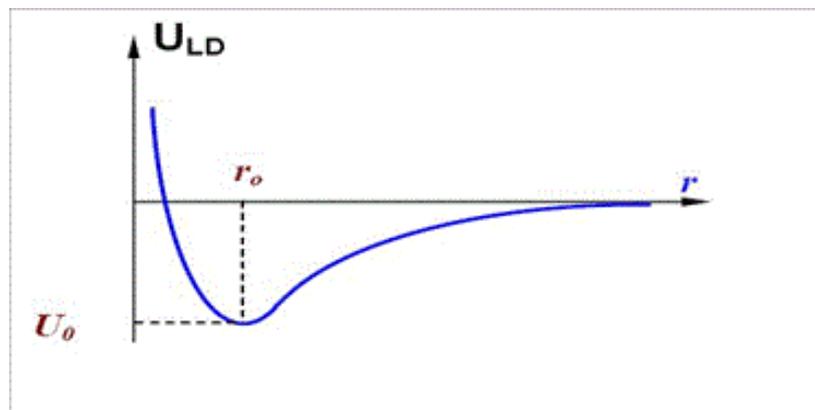

Fig. 4 – The potential energy of interatomic interaction
depending on the distance between atoms

As an example, Raman spectra of cadmium sulfide are presented in Fig. 5. Spectra contain a band corresponding to the $A_1(LO)$ phonons (the electrons in CdS interact most strongly with just such phonons). It is seen that in the case of a lattice subjected to compressive strain, the line is shifted by several inverse centimeters to the higher energies spectral region.
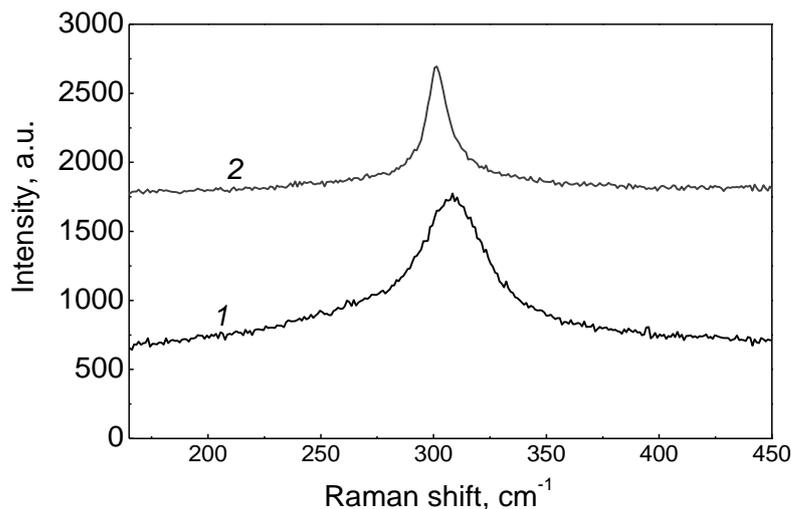
Fig. 5 – Raman spectra of CdS with (curve 1) and without (curve 2) compression strain

Raman spectroscopy of defective crystals. Until now, when considering the Raman scattering, we have assumed the ideal crystal. The presence of the crystal structure defects leads to the following features in the Raman spectra:

1. Appearance of new lines (bands), corresponding to local vibrational modes of defects. For example, in the case of the hydrogen molecule in the silicon lattice a line with position from ~4152 cm^{-1} to ~4158 cm^{-1} (depending on what position in the lattice molecule occupies) is observed (for comparison, the Raman line at 4161 cm^{-1} corresponds to the free hydrogen molecule).

2. Relaxation of the $q = 0$ conservation law for a one-phonon scattering. This effect is illustrated in Fig. 6. As mentioned above, both absorbed and emitted photons can not change the wavevector of the electron, so only phonons with $q = 0$ participate in the one-phonon scattering (Fig. 6a). If the defect concentration is high, the probability of the process illustrated in Fig. 6b increases. In this case, the electron scattering by a defect compensates for the change of the electron momentum resulting from its interaction with phonons with $q \neq 0$. A result of such scattering the photon energy will be reduced by the value equal to the energy of phonon with $q \neq 0$. Since the density of the phonon spectrum increases sharply at the edges of the Brillouin zone, the largest contribution to this scattering is given by phonons with wave vectors close to the Brillouin zone edges. Therefore, these phonons are called disorder activated zone-edge (DAZE) phonons.

As a classic example of manifestation of disorder activated phonons in Raman spectra one can consider so called D band of sp^2-carbon (graphite, graphene, carbon nanotubes). The phonon dispersion law for sp^2-carbon materials is shown in Fig. 7a. Because the number of atoms in the cell is equal to two, there are three acoustic and three optical oscillation branches. Oscillations corresponding to oTO branch are inactive in Raman spectra, frequencies of LO and iTO branches at $q = 0$ are the same, therefore, in the Raman spectrum of sp^2-carbon only one one-phonon band must present (so called G-band, 1582 cm^{-1}, Fig. 7b).

However, the experiment shows that a so-called D-band at ~1350 cm^{-1} can additionally be observed along with the G-band in the Raman spectra, and its intensity increases with the disorder degree in the material. This D-band is originated from the scattering by phonons with $q \neq 0$. It is obvious that intensity ratio of D- and G-bands can serve as a measure of a defectness of a carbon material.
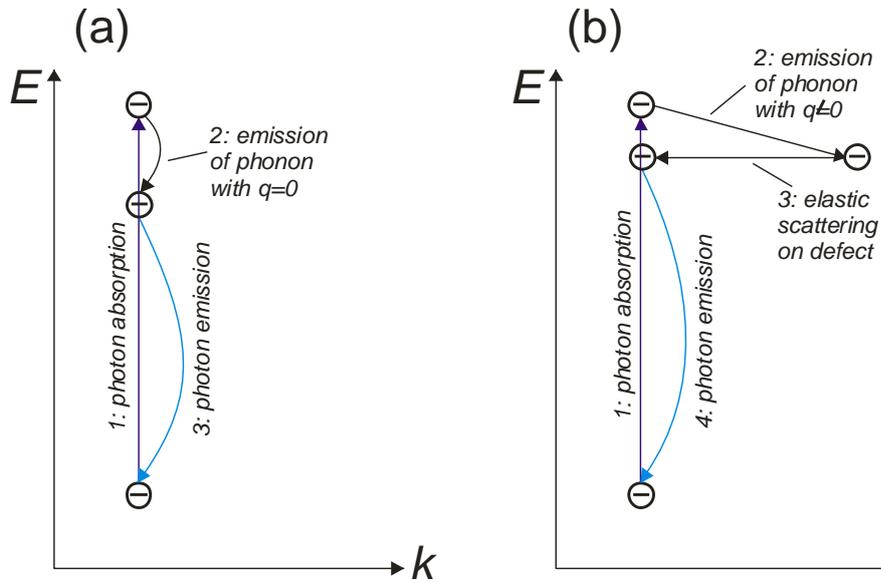
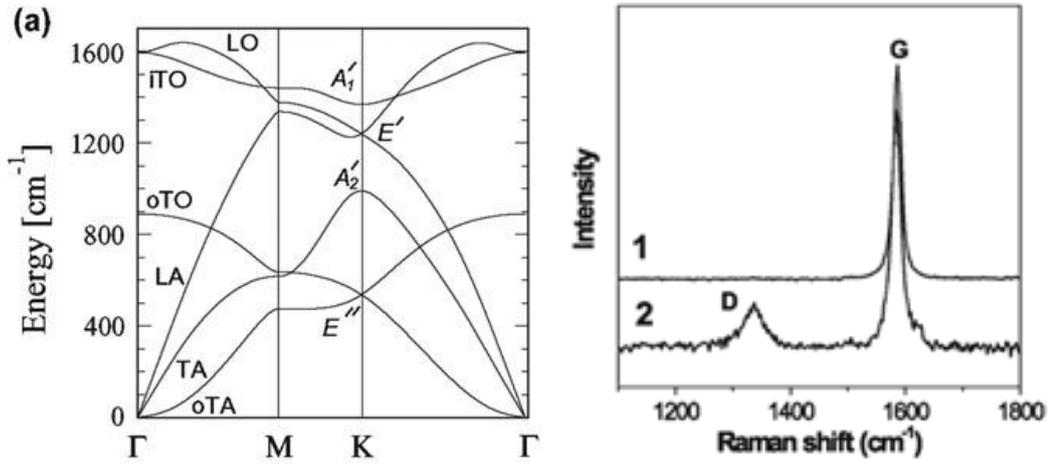Fig. 6 – Raman scattering without (a) and with (b) participation of defect

Fig. 7 – Phonon dispersion curves of sp^2-carbon (on the left) and Raman spectra of graphite
(on the right): 1 – high quality sample, 2 – sample with a high defectness

Raman spectroscopy of nanostructured systems

As mentioned above, only phonons with a wave vector close to zero are taking part in the one-phonon scattering. At the same time, it follows from the uncertainty relation that the uncertainty of the wave vector Δq increases when size of the crystal d is decreasing:

$$\Delta q \cdot d \geq 1. \tag{22}$$

Therefore, when the crystal size is reducing to a value comparable to the lattice parameter, the uncertainty of the phonon wavevector becomes comparable to the size of the Brillouin zone (Fig. 8a). The uncertainty of the phonon frequency (energy) corresponds to this uncertainty of its wavevector. As the optical phonon frequency decreases with increase of distance from the center of the Brillouin zone, a low-energy asymmetric broadening of the Raman lines shown in Fig. 8b occurs, and the broadening degree increases as the size of nanoparticles is reducing.
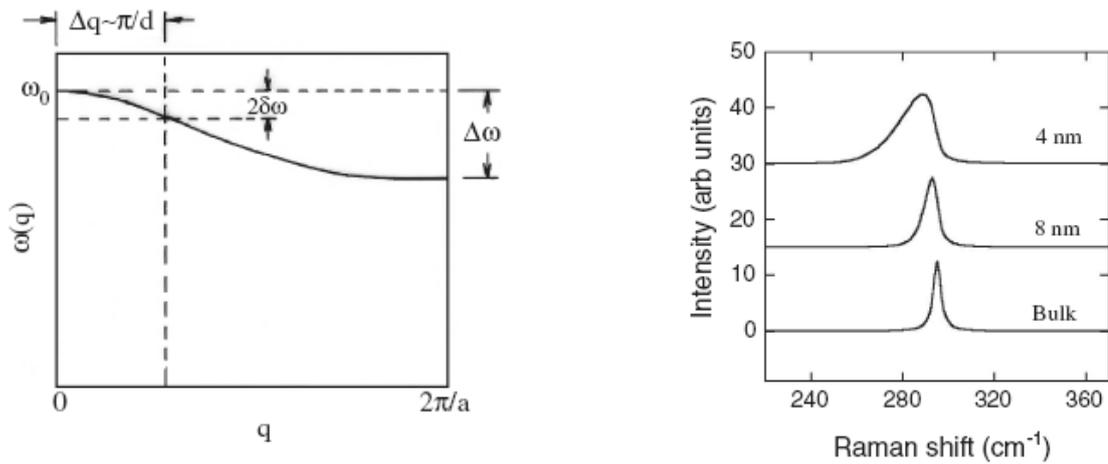
Fig. 8 – Schematic representation of the dispersion law for optical phonons (a) and the transformation of the contour of one-phonon line with a decrease in the size of nanoparticle (b)

Experimental technique of Raman spectra measurement.

In accordance with relation (10), it is necessary to know the wavelength of the incident and the inelastically scattered radiation to calculate the Raman shift. The incident radiation must be maximally monochromatic because otherwise the width of Raman lines will be determined not by the properties of the investigated object, but by the spectral composition of the exciting light. For this reason, for the excitation of Raman spectra one use currently lasers that allows to obtain a radiation, the spectral width of which does not exceed (in the wavenumber scale) ~1 cm^{-1}.

To disperse the scattered light, one use spectrometers based on diffraction gratings. Increase of the grating dispersion enables one to increase a spectral resolution, but reduces the detectability (the ability to detect weak signals in noise).

Photodetector is one of the most important elements of the Raman spectrometer. Deep-cooled CCD matrixes are widely used today as photodetectors. For modern silicon-based CCD matrices dark currents are equal approximately 10^{-3} electrons per second per pixel. A dispersing element (diffraction grating) "expands" the scattered radiation onto CCD matrix, as a result of that the radiation of a certain wavelength falls on each of its pixels. This makes it possible to register a certain part of the spectrum, the width of which is determined by the geometrical dimensions of the matrix, the configuration of optical system in general, as well as the dispersion of the grating.

When working with heterogeneous objects, the necessity to obtain the Raman spectrum from a limited area of the investigated sample occurs frequently (the same applies to the photoluminescence spectra). In this case, one use so-called confocal spectroscopy. Its principle is demonstrated in Fig. 9. When using nonconfocal spectrometer (Fig. 9, left), radiation generated at different points of the investigated object falls into detector. Confocal spectrometer is different by introduction to the special scheme a special slit (confocal aperture), which transmits only the radiation arising in a limited region of space (Fig. 9, right).
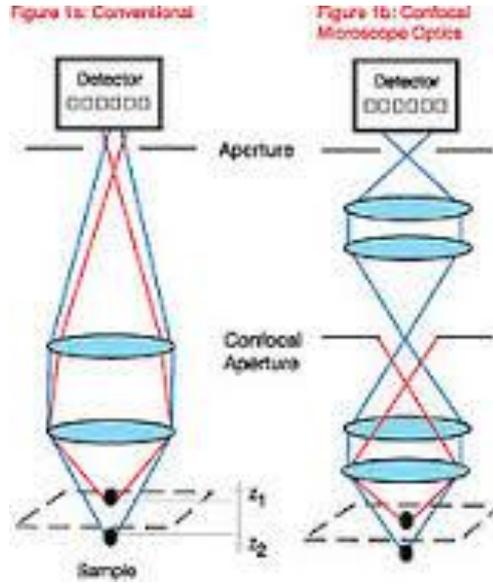
Fig. 9 – Principle of the confocal spectroscopy

Tip-enhanced Raman spectroscopy. As is seen from Fig. 9, in the case of confocal spectrometers the spatial resolution is determined by the size of the area, where laser radiation is focused. In turn, the size of this area is limited by diffraction phenomenon. Is known from optics, that the minimum diameter of the region, into which the radiation with a wavelength λ can be collected is defined by the relation

$$D = \frac{1.22\lambda}{NA},$$
(16)

where *NA* is a numerical aperture of the objective, which, as is known from optics, can not be greater than unity (immersion lenses are an exception). Thus, the spatial resolution of a confocal spectroscopy is of micrometer order. This is quite sufficient for mapping of many types of objects, as example, cells. However, the development of new fields of knowledge, in particular, nanotechnology stimulates the search for ways to increase the resolution of spectroscopic methods.

To improve the spatial resolution of the Raman spectroscopy, the phenomenon of plasmon resonance is currently widely used. As is known, free electrons in metals are characterized by a so-called plasma oscillation frequency. Quanta of energy of such oscillations are called plasmons. If the frequency of the incident electromagnetic wave is equal to the frequency of the plasma oscillations, the resonant excitation of plasmons occurs. This phenomenon is called plasmon resonance. This leads to a local enhancement of the electric field of the incident wave. The area in which there is an amplification of the electromagnetic field has a size not exceeding one – two tens of nanometers. Plasmon resonance frequency for objects with dimensions comparable or larger than the wavelength of light is uniquely determined by the concentration of free electrons *n*:

$$E_p = \hbar\omega_p = \hbar e \sqrt{\frac{n}{m\varepsilon_0}},$$
(17)

where *e* is elemental charge.

For nanoscale metal particles a frequency shift of the plasmon resonance in comparison with massive material occurs. In this case the plasmon resonance position depends on the size of

the nanoparticles, their shape and mutual arrangement that allows to "tune" it to the desired wavelength.

The local enhancement of electromagnetic field when plasmon resonance is realized can be used to increase the spatial resolution of the Raman (and photoluminescent) spectroscopy. This is illustrated in Fig. 10. A metal probe is brought to the sample surface. As a result, if the optical system is excited, an area with an enhanced electromagnetic field occurs near the sample surface. The dimensions of this region are approximately two orders of magnitude smaller than the excitation region determined by the diffraction limit. The considered above method to increase the spatial resolution of Raman spectroscopy is called Tip Enhanced Raman Spectroscopy (TERS).

Note that the theoretically possible limit of the Raman signal enhancement using plasmon resonance is equal to 10^{14}, In practice, enhancement of the order of 10^{10} is reached.
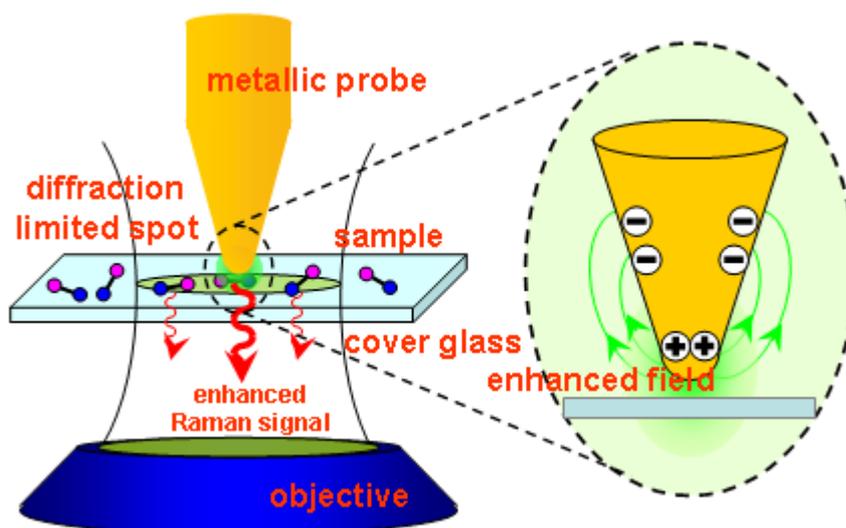

Fig. 10 – Improvement of a spatial resolution of confocal spectroscopy by TERS

Description of the laboratory setup

For the measurement of the Raman spectra a confocal Nanofinder HE (LOTIS TII, Belarus – Japan) spectrometer is used. One of four solid-state lasers emitting at 355 nm ($\hbar\omega_i = 3.49$ eV), 473 nm ($\hbar\omega_i = 2.62$ eV), 532 nm ($\hbar\omega_i = 2.33$ eV) and 785 nm ($\hbar\omega_i = 1.58$ eV) can be used for excitation of the samples. Scattered light is dispersed by one from three diffraction gratings, which provide a spectral resolution of ~3 cm^{-1}, ~1 cm^{-1}, ~0.3 cm^{-1}, respectively. Система поляризаторов позволяет выделять из рассеянного излучения составляющие, вектор поляризации которых параллелен либо перпендикулярен поляризации падающего излучения. Spectral calibration is performed using a built-in gas-discharge lamp, спектр излучения которой представляет совокупность узкий линий, положение которых известно. Для фокусировки возбуждающего излучения на образце используется один из четырех объективов, имеющих числовую апертуру от 0,15 до 0,95.

Tasks and the order of work execution

1. Acquaint with the scheme of the spectrometer and its operations manual.
2. To measure the Raman spectra of the samples issued by the teacher.
3. Taking into account the sample legend, to extract the maximum possible information from the obtained data.

Test questions

1. In the Raman spectrum of silicon a fairly narrow band ~520 см$^{-1}$ corresponds to one-phonon processes, and a broad band from 900 to 1000 cm^{-1} corresponds to the two-phonon ones. Why the position of the two-phonon band is not multiple of 520 cm^{-1}? Why the two-phonon band has a much larger width?

2. Diamond, silicon and germanium have the same crystal lattice type. For what of these materials one-phonon line is characterized by a maximum Raman shift? Why?

3. How the scattering by acoustic phonons can manifest itself in the Raman spectra?

Instructions for report execution

The report should contain:

1. Title of the work.

2. Name of students who performed the work.

3. Introduction, where the aim of investigation is formulated.

4. Short summary of the theory explaining the physical nature of the investigated effects, meaning of physical quantities and measured dependencies.

5. Methods of investigation: description of the experimental setup and the objects under investigation, as well as estimation of inaccuracies should be given.

6. Experimental results and their discussion. Based on the experimental data, the main regularities should be marked and physical phenomena underlying them should be analyzed.

7. Conclusions. Critical analysis of the results should be contained here.

Recommended literature

1. Ю, П. Основы физики полупроводников / П. Ю, М. Кардона. – М.: Физматлит. – 202. – 506 с.