

Raman spectroscopy

1. DESCRIPTION OF THE RAMAN EXPERIMENT

1.1 General Description

Raman spectroscopy is a technique for observing vibrational, rotational, electronic and other low-frequency modes in a system. It relies on inelastic scattering (i.e Raman scattering) of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light induces transitions between different energy states in crystals or molecules, resulting in an energy loss (Stokes process) or an energy gain (anti-Stokes process) in the scattered light [1]. These energy shifts of the photons correspond to specific excitations in a material. They are detected by a special optical spectrometer.

Light can interact with matter in a number of different ways. Refraction, reflection and absorption, that you are familiar with, are the most common ones. Refracted light changes direction, which is used in lens and prism optics. Absorbed photons disappear, giving off their energy to the absorbing material. During reflection light bounces off the surfaces or interfaces of materials. When thinking of light in terms of photons, reflection from surfaces is a type of scattering. There are other types. You are probably familiar with Compton scattering when high energy photons scatter from free electrons exchanging energy and momentum with them. This lab focuses on Raman scattering, where visible light interacts with crystals while exchanging energy with them. The simplest (but not quite correct as described below) way to understand Raman scattering is to imagine that a photon gives off some but not all of its energy to the material. In the process the photons do not disappear, but lose or gain some energy, i.e. they change their wavelength. By measuring the spectrum of the Raman-scattered light one can learn a great deal about the excitation spectrum of the material. Raman scattering is used widely in chemistry to identify materials based on their Raman spectra. In physics Raman scattering is used for investigating a wide variety of materials. It provides information about how atoms vibrate and about electronic excitations. In this lab we will perform experiments on two quantum materials, Silicon, which is widely used in electronics and YBaCuO, which is closely related to high temperature superconductors.

1.2 Basic Theory

Raman scattering can be understood on an intuitive level starting from basic quantum mechanics. Due to Heisenberg energy-time uncertainty principle, a photon can be absorbed without conservation of energy as long as it is emitted a short time after. This process is called virtual absorption and the shortly-lived (virtual) excited state is called the intermediate state. Most photons that are absorbed like this are reemitted a very short time later with the same wavelength and no excitation in the material is created or destroyed in the end. This process is called Rayleigh scattering. It actually interferes with Raman measurements and Raman spectrometer we are going to use is designed to filter it out.

During Raman scattering the intermediate virtual state is involved in the same way, but wavelength of the emitted photon is different from the incident one. In this case the energy has to be conserved between the initial and the final state, because both the incident and scattered photon have a long lifetime. In order to conserve energy an excitation is created inside the material. For example an electron can jump into a different orbital or an atomic lattice vibration is induced or annihilated. The energy of this excitation must equal to the difference between the incident and scattered photon. If there is no excitation that would satisfy this rule, then the scattering process is impossible. Therefore, Raman scattering can occur only if the difference between the incident and scattered photon energies is equal to the energy of an excitation inside the material. Let's see how this works starting from the quantum mechanical Hamiltonian describing the interaction of light with electrons. If you don't understand the following equations, you will still be able to do the lab.

First, consider the coupling between photons and electrons. The hamiltionian is shown as follows [2][3]:

$$\hat{H} = \sum_i \frac{[\hat{p}_i + e\hat{A}(\vec{r}_i, t)/c]^2}{2m} = \hat{H}_0 + \hat{H}_1 + \hat{H}_2 \quad (1)$$

$$\hat{H}_1 = \sum_i \frac{[e\hat{A}(\vec{r}_i, t)/c]^2}{2m} = \frac{e^2}{2mc^2} \int d\vec{r} \rho(\vec{r}) \left| \hat{A}(\vec{r}, t) \right|^2 \quad (2)$$

$$\hat{H}_2 = \sum_i \frac{e}{2mc} (\hat{p}_i \cdot \hat{A}(\vec{r}_i, t) + \hat{A}(\vec{r}_i, t) \cdot \hat{p}_i) = \frac{e}{c} \int d\vec{r} \hat{j}(\vec{r}) \cdot \hat{A}(\vec{r}, t), \quad (3)$$

where \hat{p}_i is the momentum operator, $\hat{A}(\vec{r}_i, t)$ is the electromagnetic vector potential, charge density operator $\rho(\vec{r}) = \sum_i \delta(\vec{r} - \vec{r}_i)$, electron particle current operator $\hat{j}(\vec{r}) =$

$\sum_i \frac{\hat{p}_i \delta(\vec{r} - \vec{r}_i) + \delta(\vec{r} - \vec{r}_i) \hat{p}_i}{2m}$, and sum is over all electrons and we omit the term without the vector potential.

As a result of one scattering event, the scattering medium makes a transition from state $|i\rangle$ to state $|f\rangle$ and the laser light from $|N_{Lk}\rangle$ to $|N_{Lk} - 1, N_{Sk'} = 1\rangle$. Here L and S are the polarization of light and k is the wavevector. Let X denote the Raman active excitation. If X is coupled to $\vec{\rho}(\vec{r})$ and $\vec{j}(\vec{r})$ and satisfies the symmetry requirements (see section 1.5), it will be Raman active. From perturbation theory, in the absence of a significant number of photons in the scattered channel, we get the following second order scattering cross section:

$$\frac{d^2\sigma}{d\omega d\Omega} = \frac{\omega_L \omega_S^3 n_S V^2}{n_L c^4} \sum_{i,f} e^{-\beta\epsilon_i} |\langle f | \chi_{LS} | i \rangle|^2 \delta(\omega_L - \omega_S - \omega) \quad (4)$$

in which

$$\begin{aligned} \langle f | \chi_{LS} | i \rangle = & \frac{Ve^2}{\omega_L \omega_S} \sum_m \left(\frac{\langle f | \vec{j}(\vec{k}_S) \cdot \vec{e}_S | m \rangle \langle m | \vec{j}(-\vec{k}_L) \cdot \vec{e}_L | i \rangle}{\omega_m - \omega_i - \omega_L - i\eta} + \frac{\langle f | \vec{j}(-\vec{k}_L) \cdot \vec{e}_L | m \rangle \langle m | \vec{j}(-\vec{k}_S) \cdot \vec{e}_S | i \rangle}{\omega_m - \omega_i + \omega_L - i\eta} \right) \\ & - \frac{e^2}{m_e \omega_L \omega_S \vec{e}_L \cdot \vec{e}_S} \langle f | \rho(-\vec{q}) | i \rangle \end{aligned} \quad (5)$$

where \hat{H}_1 contributes to the first order expansion and \hat{H}_2 to the second order term, \vec{e}_L and \vec{e}_S are polarization vectors of the incident and scattered photons respectively, ω_L and ω_S are their frequencies, $|i\rangle, |f\rangle$ and $|m\rangle$ are the initial, final and (virtual) intermediate electronic states of second order perturbation theory, and ω_i, ω_f and ω_m are their energies. η is a positive infinitesimal, which is replaced by the damping parameter for state $|m\rangle$, where appropriate n_L and n_S are the refractive index at ω_L and ω_S , m_e is the mass of the electron.

1.3 Notation for describing polarization geometries

Notation for describing the result of a Raman experiment is a(bc)d, where a(d) is direction of momentum of incident (scattered) photons, and b(c) is the direction of polarization of incident (scattered) photons. For example, $z(xy)\bar{z}$ means that momentum of the incident photon is in the z direction, of scattered photon in the z direction; incident photon is polarized along x, scattered along y. In our experiment we use a quasi backscattering geometry, so the polarization configuration is $z(ab)\bar{z}$. We just use ab below for simplicity.

1.4 Resonant Raman Scattering

From equation (5), when either of the denominators goes to zero, we will get the resonant Raman Scattering. At the resonance condition, Raman signals are greatly enhanced.

1.5 Selection Rules

Crystals are highly symmetric. There are two types of symmetries in crystals: Discrete translational symmetry and discrete point group symmetry. The translational symmetry means that certain translations take the crystal into itself. In addition certain rotations, reflections, and inversion performed while keeping one point fixed also take the crystal into itself. For example, in a simple cubic crystal 90 degree rotations around any one atomic position take the crystal into itself, etc. Turns out that these symmetry operations have deep consequences for the physical properties of materials, including for what is observed in the Raman spectra. The formal theory is rather involved and is outside the scope of this lab.

For our purposes it is important to realize that the wavelength of both incident and outgoing light is much longer than the interatomic distances, so one can think of every unit cell sitting in the oscillating effectively spatially uniform electric field of the incident light plus the electric field of the Raman-scattered light. Now, for example, consider an atomic vibration in a crystal with inversion symmetry induced by the Raman process. Inversion takes the equilibrium structure into itself, however, if you think of the phonon as a deviation from the equilibrium structure, inversion can take the phonon into minus itself (odd phonon) or into itself (even phonon) depending on the specifics of how the atoms vibrate.

Photons in the incident and scattered light together are even under inversion, because the relative angle between their polarizations does not change. The scattering process starts out with the incident electric field only, and ends with the phonon and scattered electric field. But the symmetry of the entire system (electric field plus crystal) has to remain the same before and after scattering. Let's consider, for example, inversion. Originally, crystal is even under inversion and the incident electric field is odd, so the total system before scattering is odd under inversion. After the scattering, if the phonon is even under inversion, the system is still odd (because the scattered photon is odd), so this scattering process is allowed. If

the phonon is odd under inversion, then the symmetry after scattering is even, and such a process is forbidden.

Each symmetry operation of the crystal imposes strict constraints on which incident/scattered photon polarization allows scattering from which phonons. Exactly how it works can only be understood based on group theory that is not a part of the standard physics undergraduate curriculum. In this lab we will explore these selection rules experimentally. As we have seen from the above example of inversion, symmetry of the combined incident and scattered photon determines which phonon is Raman active and which is not.

Another symmetry operation that is instructive to consider is reflection. If the incident photon and scattered photon polarizations are parallel to each other and both are in the reflection plane of the crystal, both photons are even under reflection. Thus only phonons that are even under reflection in the same plane could be Raman active. If they are odd they would not be. Note that one symmetry is sufficient to make the phonon Raman inactive. For example, if the phonon is even under reflection but not under inversion, then it will not be Raman active for parallel polarizations of incident and scattered light. So wrong parity under just one symmetry operation is sufficient to make the phonon Raman-inactive.

As you may have guessed, these symmetry constraints are severe, and most simple crystals have very few if any Raman active phonons. To see a lot of phonons in Raman scattering, one must look at crystals with many atoms in the unit cell. The best way to see how these selection rules work without getting too deep into group theory is to measure real materials.

In this lab we will measure one relatively simple crystal that has only one Raman active phonon, silicon, and one complicated crystal that has many Raman active phonons, $\text{YBa}_2\text{Cu}_3\text{O}_6$ (YBCO). These two compounds play a special role in science and technology. Silicon is at the heart of all electronics and YBCO belongs to the family of high temperature superconductors.

This course would only provide a brief introduction. If you are interested, you may refer to Reference [2] for more information.

1.6 detailed balance

At finite temperatures $T > 0$, inelastically scattered light is found on either side of ω_0 . As a consequence of time-reversal symmetry and phase-space arguments, the energy gain (anti-

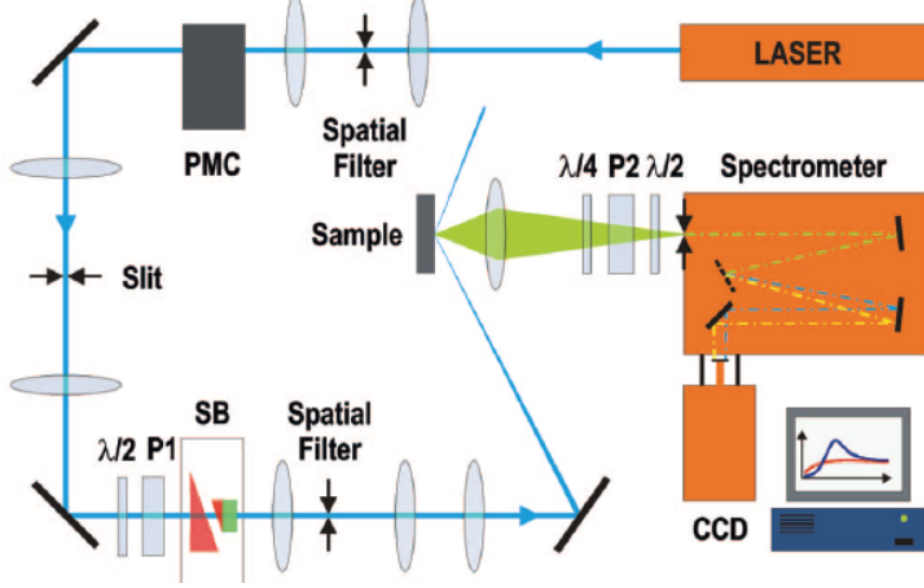


FIG. 1. Schematic drawing of light path

Stokes) and loss (Stokes) spectra are related by the principle of detailed balance (equivalent to the fluctuation-dissipation theorem)[2].

$$\frac{\dot{N}_{AS}}{\dot{N}_{ST}} = \left(\frac{\omega_0 + \omega}{\omega_0 - \omega} \right)^2 e^{-\beta\omega} \quad (6)$$

in which, $\dot{N}_{ST(AS)}$ is the rate of photons per unit time collected on the Stokes (anti-Stokes) side, and ω is the energy transferred to the system.

2. ALIGNMENT

sample alignment

Theoretically speaking, an ideal apparatus for Raman scattering is shown in figure 1 above. For more details, you may refer to Reference [2].

Our experimental setup is much simpler, as shown in Figure 2 below. When aligning the apparatus, we need to meet the following requirements:

1. Light incident on P1 must be perpendicular to its surface.
2. Light should go through the middle of L as accurate as possible.

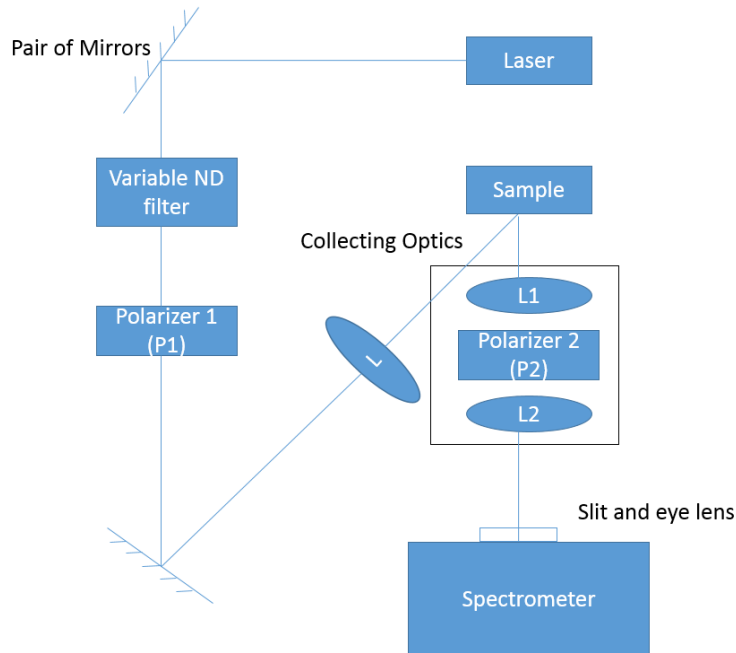


FIG. 2. Senior Lab experimental setup

3. Guide the laser onto the sample. Move the sample backward and forward so that it shows a clear image in the periscope.
4. Try to rotate the sample so that the specular reflection is outside the collecting optics.
5. Adjust the steering mirror so that the image of the laser spot on the sample is at the center of the periscope view. (remember to use an attenuator before looking through the periscope when the laser is on. Your eyes might hurt if you don't attenuate the laser.)
6. Never adjust L2, but you may adjust the height of L1 if necessary. (Don't rotate it.)
7. When finishing collimating the apparatus, you should be able to see a light spot on the sample through the periscope, with the periscope open and the slit smallest.

operation of the spectrometer

The Spec spectrometer consists of a filter stage and a final stage (Figure 3). The filter stage is used to remove the elastic light, and the final stage is used for spectroscopic analysis.

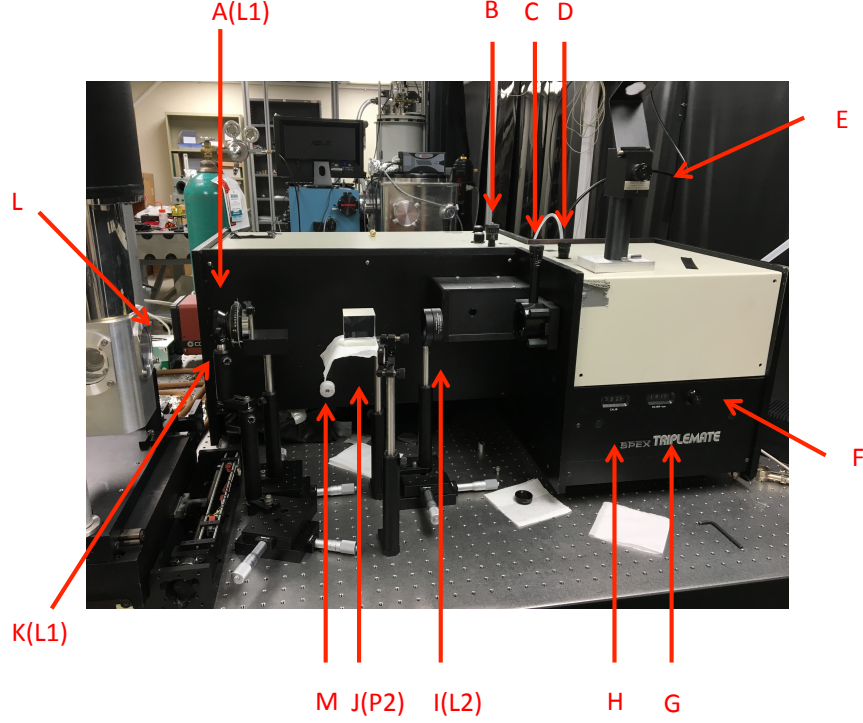


FIG. 3. The picture of the spectrometer. (A) camera lens (B) final slit (C) entrance slit (D) intermediate slit (E) periscope (F) filter stage knob (G) filter stage counter (H) final stage counter (I) lens 2 (J) polarizer 2 (K) focusing lens (L) sample (M) final stage knob

1. set the entrance slit width (C).
2. set the final slit (B) width to the same size as the entrance slit.
3. set the intermediate slit (D) wide open.
4. move the final stage knob (M) such that the laser line is in the left region of the CCD.
This knob adjusts the grating in the final stage very slowly, so be patient.
5. move the filter stage knob (F) to longer wavelength (look at counter G) until the laser line disappear on the CCD.
6. put a green notch filter in front of the entrance slit. (Caution: **Never increase the laser power unless the notch filter is placed**)
7. lift the periscope (E).

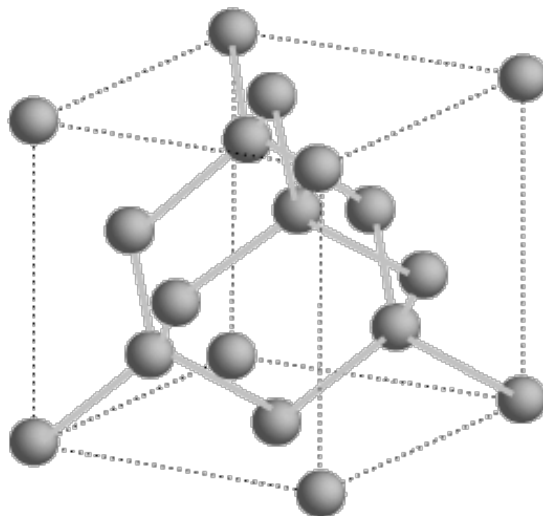


FIG. 4. Silicon crystal structure

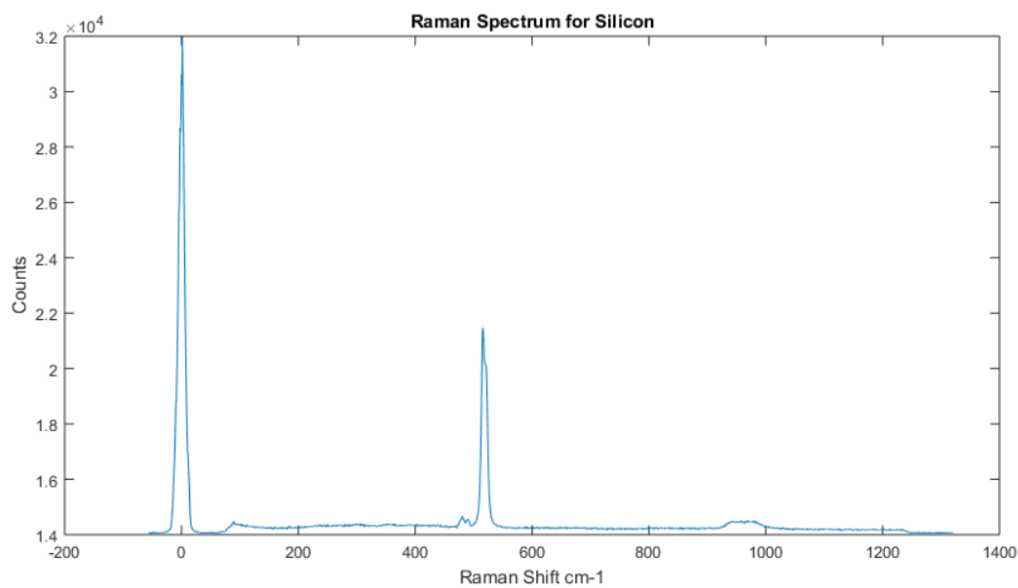


FIG. 5. Raman Spectrum of Silicon

8. start acquisition.

3. SPECTRUM OF SILICON

Spectrum is as shown on the next page.

The laser used here is 532 nm.

The formula for calculating Raman Shift is $\delta = \frac{1}{\lambda_0} - \frac{1}{\lambda_1}$, here λ_0 is the incident wavelength (laser wavelength) and λ_1 is the scattered wavelength. In the figure 4, we can see that the peak at 0 cm^{-1} is the laser peak. The sharp peak at about 515 cm^{-1} is a phonon peak. The broad peak at about 960 cm^{-1} is possibly a electronic excitation peak. We also note that there is a side peak at about 480 cm^{-1} . It is the peak of the room light and should not show up. It shows up because the dark room is not kept well.

experimental step

1. Follow section 2 to align the silicon sample.
2. Open the entrance slit to 100 μm . Smaller entrance slit gives a better resolution but lower intensity.
3. Start acquisition.

4. INTENSITY CALIBRATION

Because the overall throughput (including collecting optics, gratings, and CCD) depends on wavelengths, we need to calibrate the intensity to make sure the peaks we identify in the original spectrum are real peaks. This calibration is important especially for temperature measurements from stokes/anti-stokes ratio and for measuring broad raman peaks like two-magnon peaks. The way to calibrate is to measure some light sources with known spectrum, like a calibration lamp in our case. The apparatus is as shown in Figure 5 above. We first pick the wavelength range that we want to calibrate. Then we measure the spectrum of Calibration Lamp in this range. Here, the lamp should run at the maximum current, and probably we will need a ND filter just in front of the slit, whose transmittance is known. We also need to use as short exposure time as possible. Then compare with the data we already have to decide the response parameters of different wavelengths. Finally, multiply original data by the parameters to acquire the real Raman spectrum.

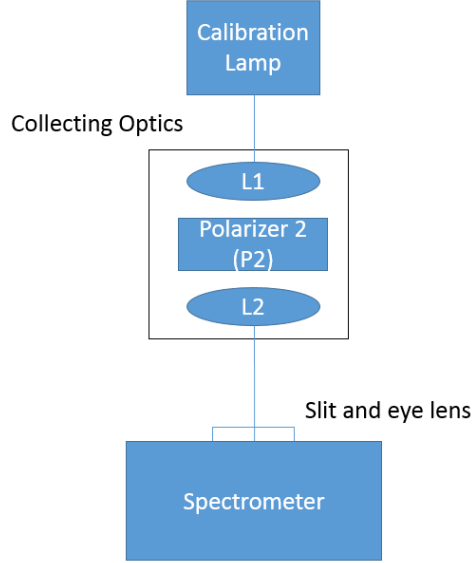


FIG. 6. Intensity Calibration Setup

experimental step

1. Put the calibration lamp to where the sample is, i.e make sure we can see the filament in the periscope.
2. Install the ND filter in front of the entrance.
3. Start acquisition.
4. Now you have everything that you need to calibrate the intensity. Think about how to calibrate the Silicon spectrum in the previous section.

5. SPECTRUM OF INSULATING YBCO

$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) is a family of compounds famous for high T_c superconductivity. The superconductivity property highly depends on the value of x , the oxygen content. YBCO is superconducting when $0 < x < 0.65$. When $x = 0.07$, YBCO establishes the highest T_c of 95 K. When $x = 1$, YBCO is insulating and does not superconduct. In this experiment we will focus on this insulating YBCO. The insulating YBCO has a tetragonal crystal structure with D_{4h} point group symmetry.

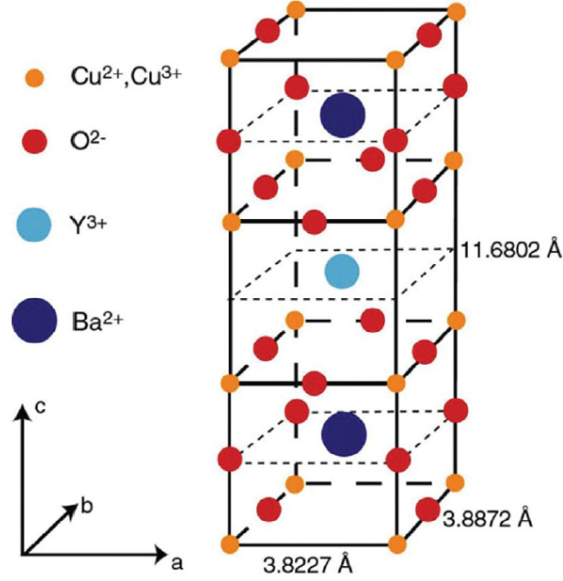


FIG. 7. YBCO crystal structure. The unit cell of YBCO consists of 3 perovskites. The middle perovskite contains Y at the center, and the top and bottom perovskites contain Ba at the center. All corner sites of the perovskites are occupied by Cu. Each Cu site is surrounded by oxygen atoms. The structure has a stacking of different layers: $(\text{CuO})(\text{BaO})(\text{CuO}_2)(\text{Y})(\text{CuO}_2)(\text{BaO})(\text{CuO})$.

Polarization analysis is important in the Raman measurement in YBCO, as different light polarization configurations can select excitations of different symmetries. You will measure the xx , $x'x'$, xy , and $x'y'$ configurations. Here the configuration xx/xy denotes that the incident laser polarization is parallel to the primitive cell in-plane crystal axes (a and b), and the scattered light polarization is parallel/perpendicular to the incident laser polarization respectively. The x' and y' directions are rotated 45° in the ab plane with respect to a and b . Note that the x -direction is along the Cu-O bond. It is perpendicular/parallel to a straight edge of the sample.

Measure phonon spectra in insulating YBCO and perform polarization analysis by measuring xx , xy , $x'x'$, and $x'y'$ configurations. We will need a polarizer to control the incident beam polarization and a film polarizer to analyze the polarization of scattered light. The figure shows how the polarizing cube selects polarizations. The polarization configurations and the sample orientation are also shown in the figure. We will need to rotate the sample by 45° for the $x'x'$ and $x'y'$ configurations.

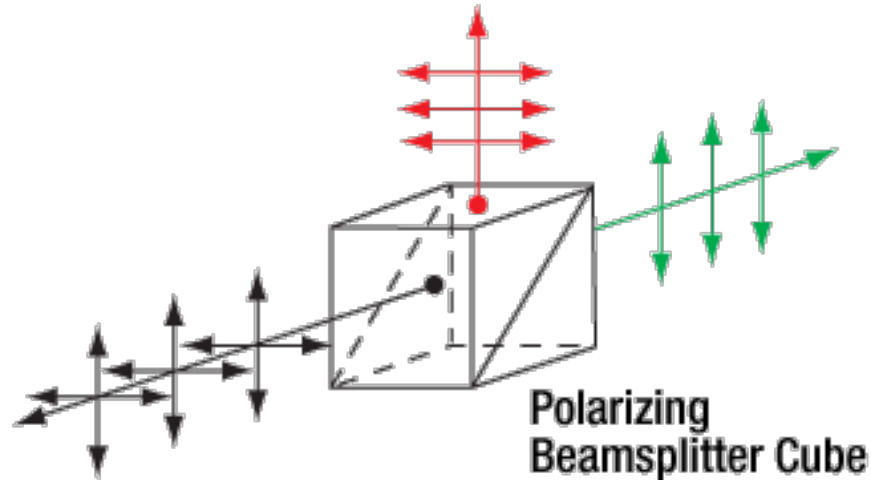


FIG. 8. polarizing beamsplitter splits the beams with different polarizations

experimental step

1. Measure phonons in the 4 different polarization configurations. Make sure that the incoming beam is perpendicular to the surface of polarizers.
2. Figure out the symmetry property of each phonon mode based on the character table (ie which phonon mode is A_{1g} ?).

6. DETAILED BALANCE (OPTIONAL)

In this experiment we will use the concept of detailed balance to measure temperature.

experimental step

1. Measure the phonons on the anti-stokes side in YBCO.
2. calibrate the intensity.
3. apply the detailed balance equation to calculate the temperature.
4. Try different powers of laser and measure the temperature again.

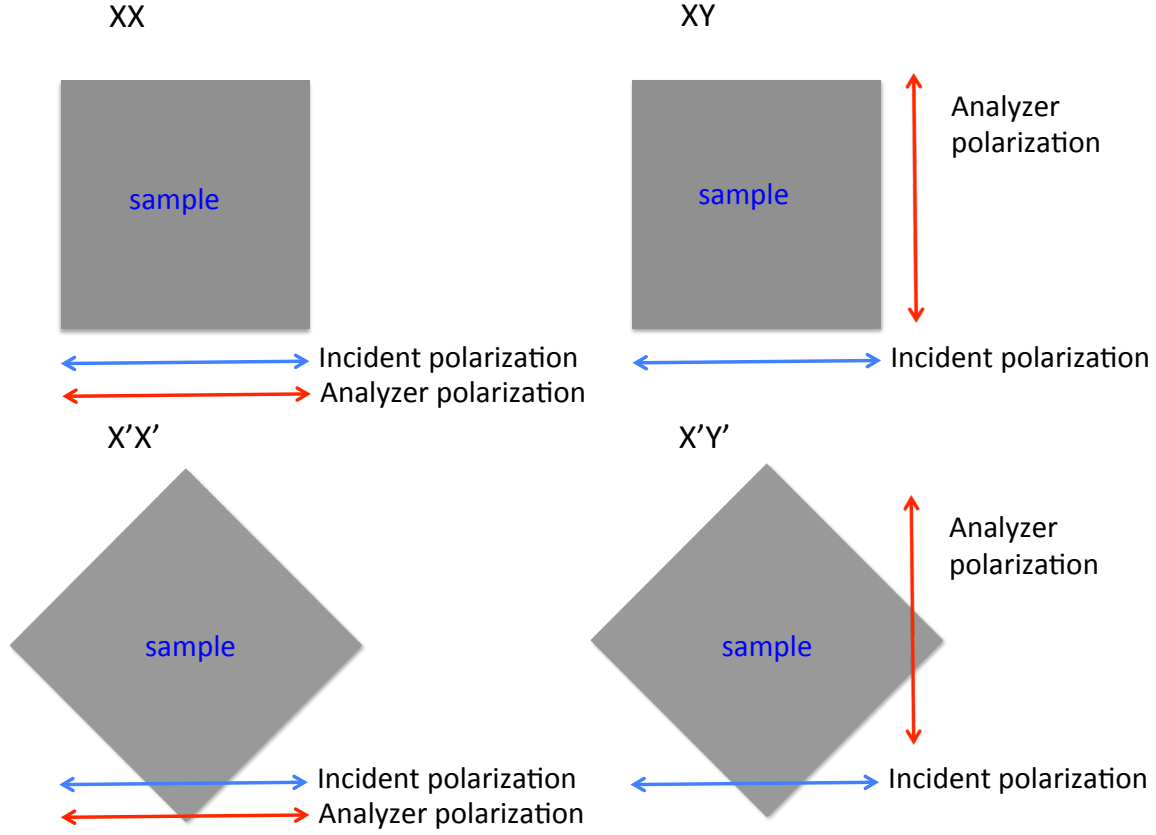


FIG. 9. sample orientations and light polarizatons

7. TWO-MAGNON SCATTERING IN INSULATING YBCO

In addition to phonons, there is a strong and broad two-magnon peak at $\sim 2700 \text{ cm}^{-1}$ in insulating YBCO. Two-magnon scattering is one of the most characteristic features in the antiferromagnetic order in the insulating cuprates. In order to cover the region of large Raman shifts, you will need to change the gratings to the ones with lower groove density. We also need to do intensity calibration to observe the two-magon peak clearly.

experimental step

1. Open the entrance slit to $500 \text{ }\mu\text{m}$ (why?). Measure two-magnon peaks in the 4 polarization configurations.
2. Calibrate the intensity of the measured spectra.

3. Figure out the symmetry property of two-magnon peak. In which polarizations does it appear?



- [1] Wikipedia. *Raman Spectroscopy entry*.
- [2] Thomas P. Devereaux and Rudi Hackl. *Inelastic light scattering from correlated electrons*. Rev. Mod. Phys. 79, 175 (2007).
- [3] Dmitry Reznik. *PhD thesis*.