Second Harmonic Generation in the Cuprate Family of High Temperature Superconductors

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Abstract

We outline and summarize the work completed in Cundiff Group during the summer of 2011 in the process of developing an aparatus to test the symmetry properties of the cuprate family of high temperature superconductors. We describe the theory this experiment is based in, purposed experimental setup, and progress toward its completion as well as future work on the project.

1 Introduction and Theory

1.1 Optical Second Harmonic Generation

Not long after the invention of the first laser in 1960, it was realized that the extreme intensities of the laser light gave a access to a new realm of physics: nonlinear optics. Franken *et al* were the first to generate a nonlinear optical effect when, in 1961, they sucessfully produced a second-harmonic signal from a piece of crystalline quartz. [1] As a brief historical aside, when this article was initially submitted, the small second-harmonic signal which was observed was mistaken for a speck of dust and famously removed from the final publication.

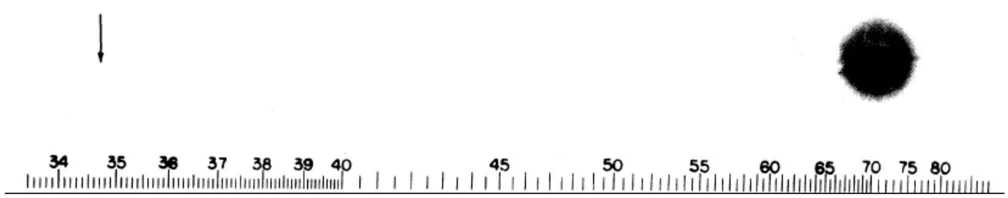

Figure 1: The first image of a second harmonic signal, generated by focusing a ruby laser on crystalline quartz. The second harmonic signal which should be visible at 347nm has been removed. [1]

These newly discovered nonlinear optical effects were quickly understood in terms of the polarization felt by the dielectric medium excited by the laser. The electrons within this medium can be approximated as simple harmonic oscillators which experience small displacements from their equilibrium positions when under the influence of a weak oscillating electric field. [2] In this case, the polarization of the medium is expressed as $P = \epsilon_0 \cdot \chi \cdot E$, where ϵ_0 and χ are the vacuum permittivity and the linear susceptibility. However, if the intensity of the incident electric field becomes large, the response of the electric polarization will be driven into the nonlinear regime.

In such a case, the simple linear relation no longer accurately describes the behavior of the medium. Instead, the polarization may be written as a Taylor expansion with each term containing an increasing electric field contribution, giving the polarization the form $P = \epsilon_0 \cdot \left(\chi^{(1)} \cdot E + \chi^{(2)} \cdot E^2 + \chi^{(3)} \cdot E^3 + ...\right)$. Here, $\chi^{(1)}$ is the linear susceptibility present in the previous incarnation of this equation, but the later terms arise due to various nonlinear effects. Specifically, second-harmonic generation (SHG) is a result of the first nonlinear term containing the second-order susceptibility tensor, $\chi^{(2)}$. A short year after the first discovery of SHG and the explanation utilizing the nonlinear polarization, Maxwell's equations were generalized by Armstrong *et al* and Bloembergen *et al* to include these nonlinear media. [3] [4]

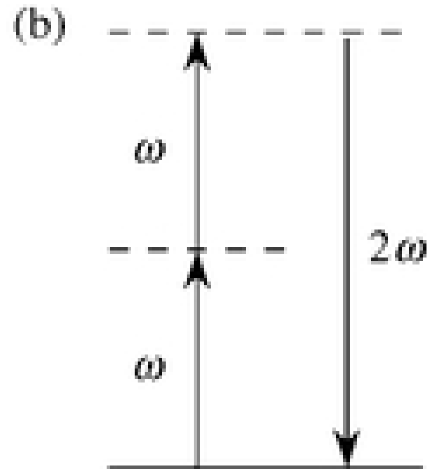

Figure 2: Energy level diagram describing the SHG process. Reproduced from Boyd. [5]

Physically, the process of SHG can be thought of as an exchange of photons between the different frequency components of the electric field. Boyd describes this as a single quantum-mechanical process in which two photons having a frequency of ω are destroyed while a single photon of frequency 2ω is created. During this process, electrons are not excited to energy eigenstates of the atom, but rather to what is a called a virtual state. This state is an intermediate state that occurs in a multi-step process which allows otherwise forbidden transitions to occur. In the case of SHG, this virtual state is an energy eigenstate of the atom combined with the energy of one or more photons from the incident electric field, refer to Figure 2. [5]

An interesting aspect of SHG is that not all media are able to generate this signal. In fact, the SH signal is dependent on the particular molecular symmetry, or lack there of, that the nonlinear media possesses. Todemonstrate, consider a nonlinear medium which is perfectly symmetric throughout, if the electric field is reversed in sign, one would expect the polarization to follow suit. However, focusing on the second order term in the polarization expansion above, $P^{(2)} = \epsilon_0 \cdot \chi^{(2)} \cdot E^2$, the second order polarization is proportional to the square of the electric field negating the above claim unless $\chi^{(2)}$ vanishes for this material. Therefore, to have SHG, the nonlinear medium must have broken inversion symmetry. In order for this to occur in the bulk of the material, the crystal structure must be non-centrosymmetric. Inversion symmetry is necessarily broken at an interface between two different crystal structures or at the surface of the sample. This dependence on symmetry led to many different experimental observations and theoretical predictions which caused SHG to develop into a powerful technique for probing the properties of a material or interface.

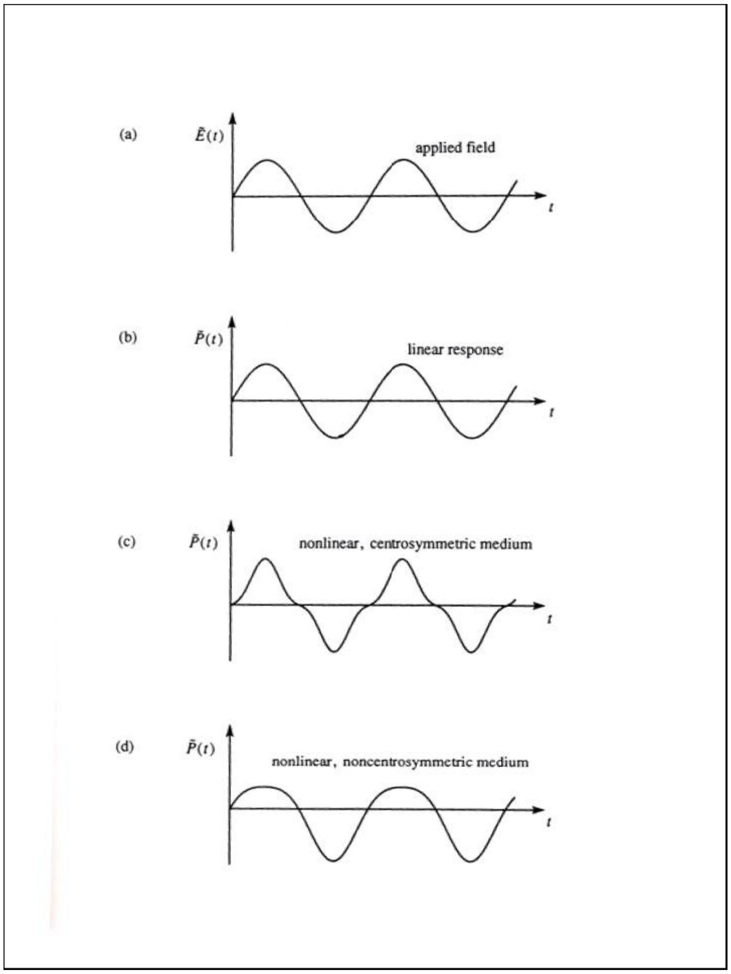

Figure 3: Optical response of charge distribution of a dielectric in an applied sinusoidal electric field (a) that induces a linear polarization (b) and a nonlinear polarization that is dependent on the particular crystal symmetry of the medium (c), (d). Reproduced from Boyd. [5]

1.2 Superconductivity and the Cuprates

The physical phenomenon known as superconductivity, the existence of exactly zero electrical resistance within a material, was first discovered in 1911 by Heike Kamerlingh Onnes when studying the electrical resistance of solid mercury when supercooled with liquid helium. Onnes observed that below about 4.2 K, the electric resistivity of mercury suddenly disappeared, allowing an electric current to flow indefinitely. [6] It was forty six years after its initial discovery that Bardeen, Cooper, and Schreiffer were able to construct a complete microscopic explanation of conventional superconductivity in what is now known as BCS Theory.

In BCS Theroy, the fundamental concept behind the superconducting phase is the formation of Cooper pairs within the lattice of a superconducting material. [7] A Cooper pair refers to the binding of two electrons by some coupling mechanism. In the case of conventional superconductors, it is understood that this coupling mechanism is an electron-phonon interaction. As electrons move through a crystal lattice, the coulomb attraction between the negatively charged electrons and positively charge nuclei causes a small deformation in the lattice structure, leading to a slightly higher concentration in positively charged particles in a small region. Another electron far away (several order of magnetude larger than the lattice spacing of the material) will feel an attraction to this displacement of nuclei and effectively couple the two electrons. [8]

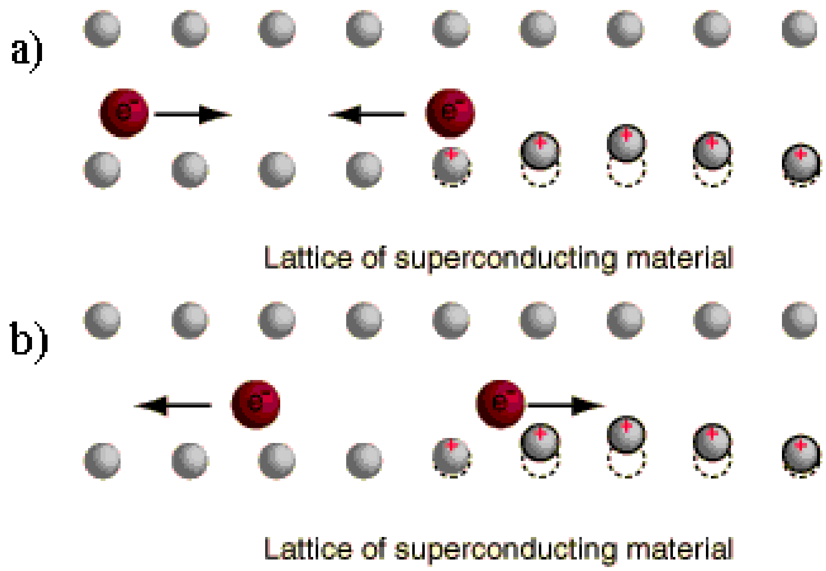

Figure 4: A simplified representation of a Cooper pair. A passing electron attract the lattice causing a ripple effect (a), a electron passing in the opposite direction is attracted to this displacement (b), effectively coupling the electrons together. [8]

This coupling allows the fermonic electrons to display bosonic behavior, meaning these Cooper pairs are all free to occupy the same (lowest) energy state. This condensation of the electronic wavefunction is what leads to the superconducting property seen in various materials. The binding energy of these Cooper pairs is only on the order of serveral milli-electronvolts and can be broken by thermal excitation unless at very low temperature. Consequently, BCS Theory places an upper bound on the superconducting transistion temperature (T_c), above which superconductivity cannot occur in materials, $T_c < 30K$. [7]

In 1986, Karl Müller and Johannes Bednorz discovered a family of cuprate-perovskite ceramic materials which have T_c above the limit predicted by BCS Theory. The first of these cuprates was lanthanum barium copper oxide, whose critical temperature match the limit predicted by BCS, $T_c = 30K$. [9] One year later, yittrium barium copper oxide (YBCO) was discovered to have a critical temperature of 90 K, the first superconducting material to have a T_c higher than the boiling point of liquid nitrogen (77 K). [10] This material opened the door to many new experimental and industrial uses for superconducting materials as it was no longer necessary to use expensive liquid helium to achieve the superconducting phase transition. However, these high-T_c superconductors are forbbidden to existence by BSC theory, meaning a new theoretical explanation is needed for these strange compounds.

Despite over two decades of experimental and theoretical research, there is still no universally accepted theory that completely describes the high-T_c behavior, though many have been proposed. One such theory is that of C.M. Varma who believes that the fundamental mechanism behind high temperature superconductivity is still the formation of Cooper pairs, though the process by which Cooper pairs form is different that that of conventional superconductors.

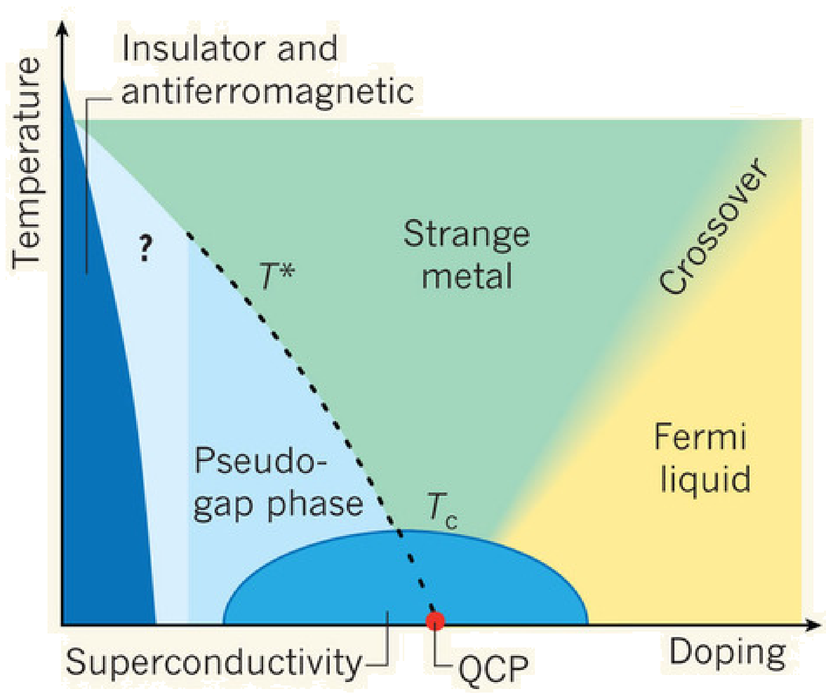

Figure 5: Varma's purposed phase diagram for the cuprate family of high-T_c superconductors. [11]

Instead of the electron-phonon interaction described above, Varma believes that electron pairing is due to interactions between an electron and magnetic excitations that begin forming when a cuprate enters what is called the pseudogap phase, which corresponds to a gradual phase change once below some temperature T^* where an energy range emerges in the curprate with very few states in it. Varma believes this phase to be a natural precursor to the superconducting state, though full superconductivity is prevented by phase fluctuations in the purposed pairing mechanism above T_c. [12]

If this proposed pairing mechanism is the correct explanation of the high-T_c supercondcuting behavior, then entering the pseudogap phase should cause these magnetic excitaions to form small current loop in the the copper oxide unit cells in one of two distinct patterns, see Figure 6. These current loops grow into larger current domains within the lattice of the cuprate. [11] The formation of these current domains causes to a distinct break in the symmetry of the cuprate lattice, meaning that if these current loops are forming when entering the pseudogap phase, it should be detectable by examining the SHG signal produced by the cuprate as a function of temperature.

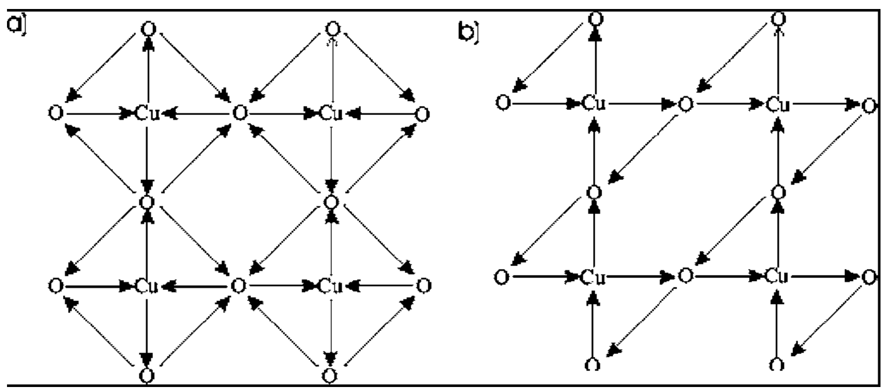

Figure 6: The two purposed current patterns expected to form in the pseudogap phase. [12]

2 Purposed Experimental Setup and Progress

Though Still in the early stages of development, a preliminary experimental setup has been determined, though subject to change as the project progresses. SHG will be used as a probe by tightly focusing a mode-locked, cavity dumped Ti:sapphire laser onto a sample of superconductor and the radiated second-harmonic light will be collected and directed into a photo multiplier tube. In addition, the incident polarization will be controllable via a linear polarizer and quarter wave plate such that near circular polarization can be obtained allowing the setup to detect the various current domains expected to form in the sample. Finally, in order to observe the purposed symmetry breaking as the cuprate transitions phase, a cryostat is used to cool and warm the samples through a temperature range consisiting of their critical temperature T_c and the pseudogap phase transition temeprture known as T^*. Before real data can be taken, there are two component of the apparatus that must be built and/or characterized: a normalization schematic of the SHG signal and the cryostat.

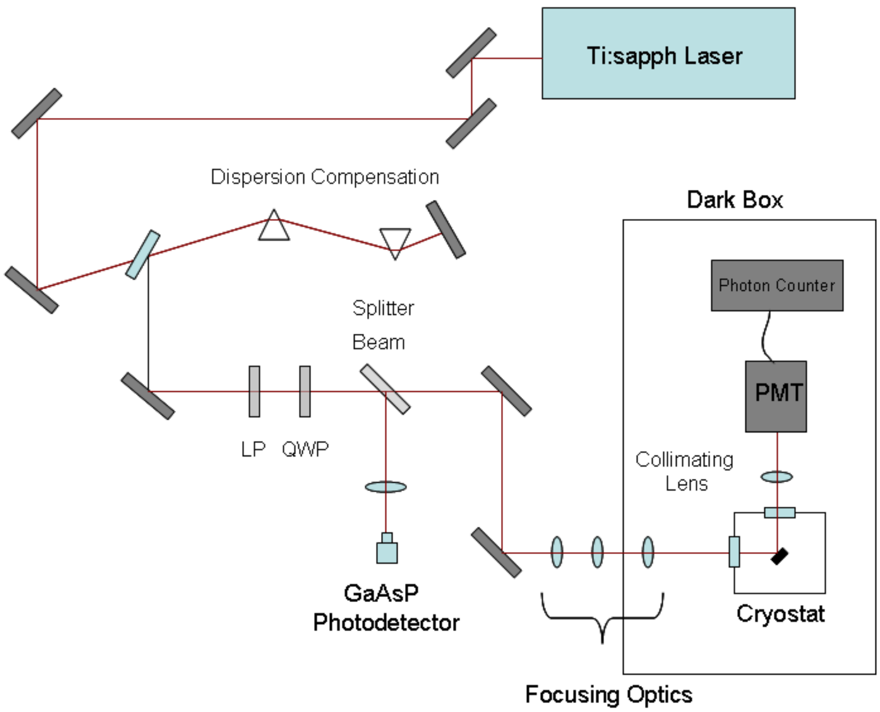

Figure 7: The purposed experimental setup.

2.1 SHG Normalization

Recall, the second order term in the nonlinear polarization expansion which controlls the second harmonic signal is given by $P^{(2)} = \epsilon_0 \cdot \chi^{(2)} \cdot E^2$. Here it is easily seen that the second order polarization is directly proportional to the square of the electric field which itself is directly related to the intensity of the laser. Using this fact and examing the wave equation for the second harmonic signal, one finds that the second harmonic signal is quadratically dependent on the intensity of the laser light. In order to account for intensity fluxuations in the laser it is necessary to develop and implement a normalization schematic which will be capable of measuring and removing these deviation in the second-harmoinc signal.

To accomplish this, the beam path of the laser will be split and one leg directed into a gallium arsenide phosphide photodetector. The optical response of this photodetector will simulate a second harmonic signal as this compound is not sensitive to light at the fundamental wavelength of the Ti:sapph laser which is about 800 nm, see Figure 8.

Due to this lack of sensitivity at 800 nm, any response seen in the detector will have to be due to another

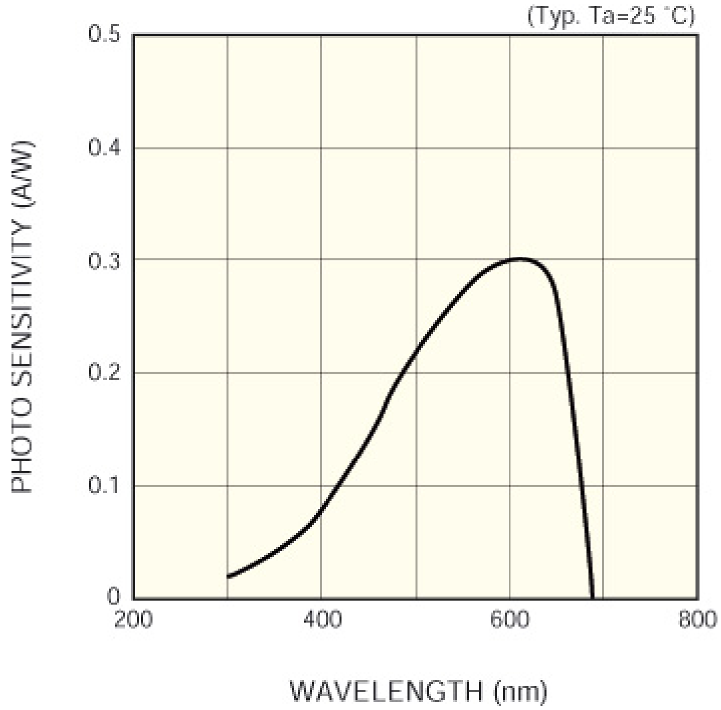

Figure 8: Photosensitivity of GaAsP, peaking at 640nm before falling off completely just before 700 nm. [13]

nonlinear optical effect known as two photon absorption. During this process, an atom is excited from its ground state by the simultaneous absortions of two photons from the incident laser beam. [5] This process, like SHG, varies quadratically with the intensity of the laser light and will be able to produce a response simulating the true second harmonic signal generated from the sample.

2.2 Cryostat Characterization

Though this experiment will be working with high temperature superconductors, room temperature superconductivity has not yet been achieved. Thus, it is necessary to have some way to cool the superconducting samples to both their proposed pseudogap and superconducting phases. To do so a CRYO Industries model 8CN optical cryostat is used. This cryostat has a four liter liquid nitrogen reservoir and a four and a half liter liquid helium reservoir, each separated by vacuum insulation which must be pumped down to 10^{-7} torr. The samples used in this experiment will be fastened to the sample mount that will sit inside the sample tube at 45° to the incident laser beam. Once inside, the samples will be cooled by the liquid helium which is pulled through a needle value where it will expand to become a cool gas absorbing and carrying heat away from the sample. The laser beam will enter the sample chamber via a pair of windows which are AR-coated for 800nm light and leave through a pair AR-coated for 400nm light to maximize the transimission of the second-harmonic signal.

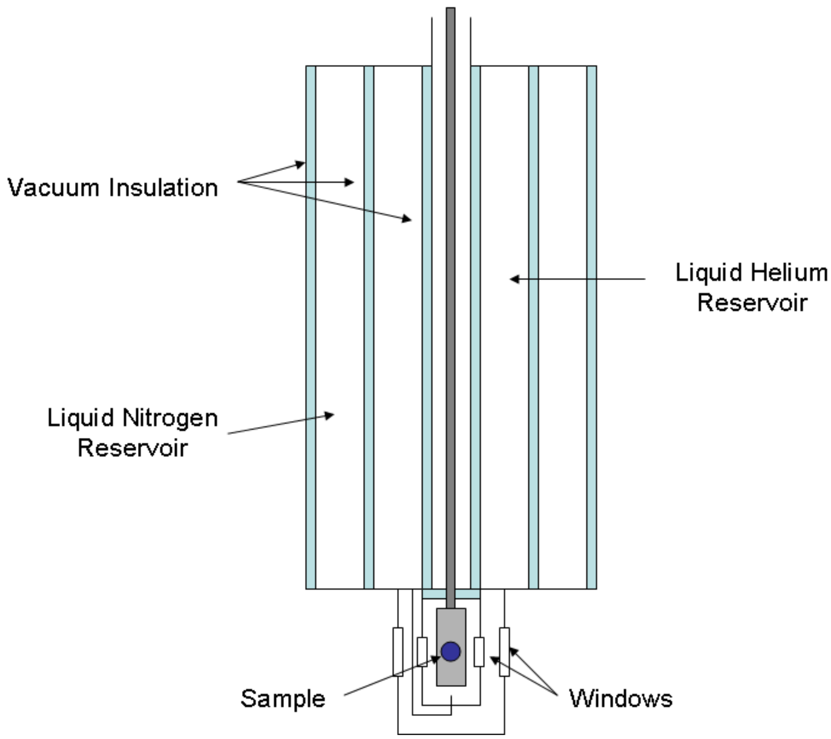

Figure 9: A simplified schematic of the CRYO Industries model 8CN Optical Cryostat.

The second-harmonic signal which is expected to be seen from these samples is extremely dependent on the polarization of the incident laser beam at the sample. Unfortunately, initial test have shown that one or both of the windows of the sample chamber have some sort of birefringent properties. Meaning that when the laser passes through this window pair, its polarization is changed in some unknown way. Thus the characterization of these windows and the compensation for their effect on the beam's polarization is necessary for the success of this project.

To detemine this effect, a new mount has been constructed which will sit inside the sample chamber and hold a pair of LEDs centered at slightly different wavelengths with polarizers fastened infront of them. The light from one LED is then directed through one of the window pairs and focused into a polarimeter. The LEDs can then be removed from the sample chamber and their polarization state can be measured without the effect of the cryostat windows. This procedure is then repeated with several different polarization states, which will allow the birefringence of the windows to be uniquely determined.

Unfortunately, the birefringence of these windows is expected to change with temperature as different

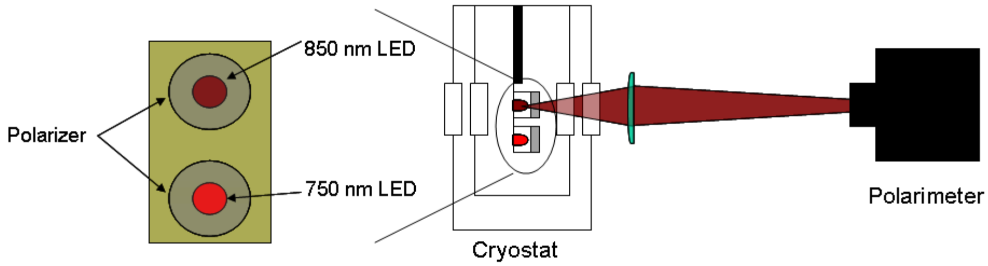

Figure 10: Basic setup of the window characterization expeiment.

stresses and strains are placed on the window as the metal around it contracts as it cools. Thus, This test will be repeated for various tempertures throughout the range of the cryostat, which is about 4K to approximately 300K. As the temperature cools, the center wavelength of the LEDs will begin to blue shift. To keep the wavelength of the light as close to 800nm as possible two different LEDs (one with a center wavelength at 780nm and the other at 850nm) are alternated between at different points in the cooling process. Strain releaving mounts have also been installed on the inner pair of windows to prevent changes in the birefringence as the cryostat cools, but their effectiveness is not yet known.

3 Future Work

There is still much to be done before meaningful measurements can be made. Though it has been confirmed that GaAsP photodetector does produce a signal which varies quadratically with the laser intensity, a calibration between the two-photon absorption and actual SHG signal still needs to be constructed. Furthermore, all four of the window pairs of the cryostat must be characterized at various temperature and a calibration table produced to correct for the added birefringence. Once these two tasks are completed, the experimental setup can be built and tested using silicon, whose second harmonic repsonse is well understood and documented, to verify everything is working properly.

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