Frequency Doubling in a KDP Crystal

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1 Introduction

Due to nonlinear atomic polarization, crystals can emit a different frequency of light than absorbed. In order to see the second order effects of atomic polarization, which cause a doubling in the frequency of the incident light, the incident light must be an intense and coherent source, like a laser. Potassium Dihydrogen Phosphate (KDP) is a crystal that exhibits these nonlinear polarization properties and is cheap to produce. In the following experiment, a KDP crystal is grown in the laboratory and probed with infrared (795nm) light from a 800mW titanium-sapphire pulsed laser to produce near UV (397.5nm) light.

2 Theory of Frequency Doubling

2.1 First Frequency Doubling Experiment

Frequency doubling, also known as second harmonic generation, was first achieved in 1961 by Peter Franken's group at the University of Michigan [1]. This experiment was made possible by the construction of the laser the year before by Theodore Mailman at the Hughes Research Laboratory in California [2]. Before the invention of laser, there was no coherent light source with high enough intensity to ellicit the effects of nonlinear atomic polarization. The group used a ruby laser and quartz crystal to achieve very low efficiency frequency doubling that was barely visible. The resultant light was put through a spectrometer to split the 694nm and 347nm light. Rumor has it that the copy editor of *Physical Review Letters* removed the dim spot of frequency doubled light thinking it was a smudge in the photo [3].

2.2 Nonlinear Polarization

When light hits a crystal, it excites the atomic dipoles. In classical optics, it is assumed that this polarization of the atoms is linear to the magnitude of the electrical field of the incident light. In reality, this polarization is a nonlinear phenomenon, but the nonlinear components are only evident for high intensity

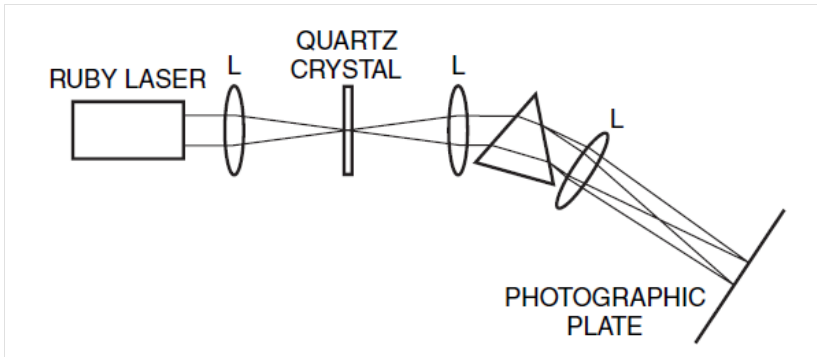

Figure 1: Experimental setup of first frequency doubling experiment. Image from [1].

and coherent light, like a laser. The nonlinear polarization of the atoms can be written as a Taylor expansion,

$$P(t) = \epsilon_0(\chi^{(1)}E(t) + \chi^{(2)}E(t)^2 + ...) \equiv P^{(1)}(t) + P^{(2)}(t) + ...$$

An incident beam of light with the electric field

$$E(t) = Ee^{j\omega t}$$

will thus cause a second order atomic polarization term of

$$P^{(2)}(t) = \epsilon_0\chi^{(2)}E^2e^{-j2\omega t} + \epsilon_0\chi^{(2)}E^{*2}e^{j2\omega t} + 2\epsilon_0\chi^{(2)}EE^*.$$

This second-order polarization term contains an oscillation term at twice the frequency of the incident light, which is proportional to the intensity of the incident light. This term is the source of second harmonic generation in certain noncentrosymmetric crystals. The last term of the second order polarization is not oscillating in time and represents a static field in the crystal, which is called *optical rectification* [4].

2.3 Noncentrosymmetric Crystals

A centrosymmetric crystal has a center of symmetry in its lattice structure, meaning there is a central atom within the crystal such that the inversion of all atoms around it would result in an identical crystal. For centrosymmetric crystals, second harmonic generation cannot occur due to potential energy arguments. The atom can be modelled as an electron attached by a spring to the nucleus. The restoring force of the nonlinear polarization can thus be written,

$$F_{restoring} = -m\omega^2x - m\alpha x^2 + ...$$

where α is a measure of the second order nonlinearity. Accordingly, the potential energy is the negative integral of this restoring force, or

$$U(x) = \frac{1}{2}m\omega^2x^2 + \frac{1}{3}m\alpha x^3.$$

A centrosymmetric crystal has a center of symmetry, so its potential energy must be symmetric, meaning

$$U(x) = U(-x).$$

The second-order polarization term equates to an odd powered term in the potential energy, which means that frequency doubling, a second-order polarization effect, cannot be present in centrosymmetric crystals [4]. KDP is a noncentrosymmetric crystal, and thus can be used for frequency doubling [5].

2.4 Phase Matching

In order for the second harmonic light to be visible in the output beam from the crystal, the atomic dipoles must be radiating constructively. This means that the output second harmonic light must be in phase with the incident laser light [1]. The incident laser light has an electric field of the form

$$E_1(t) = E_1 cos(\omega t - k_1 r)$$

and the output frequency doubled light has the electric field

$$E_2(t) = E_2 cos(2\omega t - k_2 r).$$

A look at the second order polarization effect causing the second harmonic light shows that

$$P^{(2)}(t) = \epsilon_0 \chi^{(2)} E^2 cos(2(\omega t - k_1 r)),$$

and thus

$$k_2 = 2k_1.$$

Since

$$k = \frac{n\omega}{c},$$

$$2k_1 = \frac{2n\omega}{c} = \frac{n(2\omega)}{c} = k_2,$$

and thus

$$n(\omega) = n(2\omega).$$

KDP is a negative uniaxial material that has a refractive index n_e along the optical axis and n_o along its other two axes. To match the refractive index of both the incident light and the second harmonic light, the incident light can be an ordinary beam and the second harmonic light can be an extrodinary beam

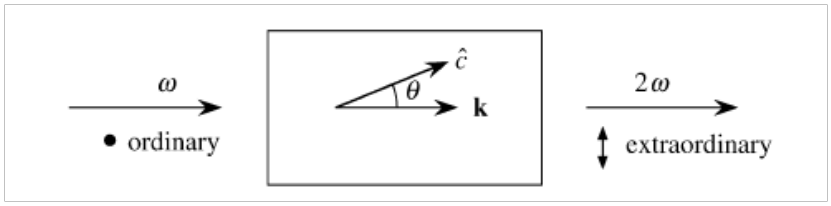

Figure 2: Phase matching in a negative uniaxial crystal. Image from [4].

with the optical axis titled at an angle to fufill the phase matching criterion (see Figure 2). Light incident at an angle θ to the optical axis will experience a refractive index of

$$\frac{1}{n^2(\theta)} = \frac{cos^2\theta}{n_o^2} + \frac{sin^2\theta}{n_e^2},$$

which lies on the ellipsoid of all possible refractive indices for the crystal [6]. In order to fufill the phase matching condition, the incident ordinary beam must have the same refractive index as the exiting second harmonic extrodinary beam, meaning

$$\frac{1}{n_o(\omega)^2} = \frac{1}{n^2(2\omega,\theta)} = \frac{cos^2\theta}{n_o(2\omega)^2} + \frac{sin^2\theta}{n_e(2\omega)^2}.$$

Replacing $cos^2\theta$ with $1 - sin^2\theta$ and rearranging this equation in terms of $sin^2\theta$ leads to

$$sin^2\theta = \frac{\frac{1}{n_o(\omega)^2} - \frac{1}{n_o(2\omega)^2}}{\frac{1}{n_e(2\omega)^2} - \frac{1}{n_o(2\omega)^2}}.$$

This is the angle at which the optical axis should be placed within the laser beam to achieve frequency doubling [4].

2.5 Intensity of Frequency Doubled Light

Including the higher-order, nonlinear terms of polarization in the wave equation will lead to a driven version of the wave equation called the *nonlinear optical wave equation*. Starting from this equation, it can be proven in a multipage proof that

$$I = I_{max} sinc^2(\frac{\Delta kL}{2}),$$

where I is the intensity of the second harmonic generation [4]. This equation relies upon a number of assumptions. First of all, it assumes the crystal is lossless. It also assumes that the incident laser light is normal to the crystal's face. Another approximation made to simplify the nonlinear optical wave equation is that the amplitude of the frequency doubled light varies slowly (compared to the wavelength) in the propogation direction. What is important to note from this equation is that the intensity of the frequency doubled light is extremely sensitive to phase mismatch between the incident light and frequency doubled

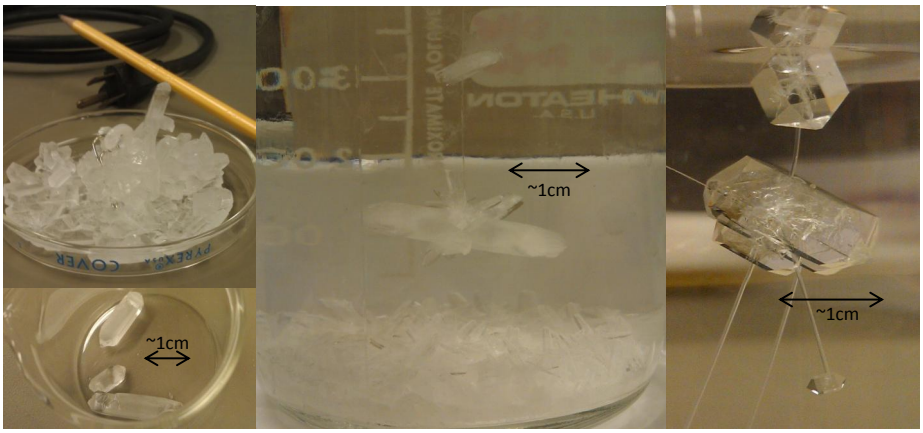

Figure 3: Cloudy crystals from the first growing attempt (left), clear, minature crystals from second growing attempt (middle), and successful growth of large, clear crystals in the third attempt (right).

light. A slight change in crystal angle or incident light angle can lead to neglible second harmonic generation.

3 Crystal Growth

I chose to grow a KDP crystal for this frequency doubling experiment because KDP is cheap and allows for easy second harmonic generation. I bought 500g of KDP for roughly 20 dollars from Avantor Performance materials (Potassium Phosphate, Monobasic, Crystal. CAS number 7778-77-0, 7100 Macron).

For my first crystal growing attempt, I boiled 500ml deionized water on a hot plate and added 150g of KDP. I hung a string weighted with a paper clip from a pencil into the 600ml beaker containing the solution. The crystals grew extremely fast, and within 24 hours I had 1cm large crystals. Unfortunately, these crystals grew too fast, causing them to have imperfections in the lattice structure, which resulted in a cloudy crystal (see Figure 3).

My second attempt to grow crystals involved reheating the saturated solution from the first attempt and dissolving the crystals in the bottom of the jar back into the solution. I took a small crystal from this original batch as a seed crystal, tied it on a string, and hung it in the new solution. Days later, I had many little clear crystals (approximately 1mm across) growing off of the cloudy seed crystal (see Figure 3). The crystals were very pointy and lacked nice, square crystalline structure.

For my final attempt, I saturated 450ml of deionized water with 120g of KDP. I hung a string into the beaker with a glass slide for weight on the bottom. I

Figure 4: The optical axis of a KDP crystal.

was careful to transfer the solution to a new beaker each day to prevent crystals from growing on the side and bottom of the glass. Five days later I had three very clear crystals, and the largest crystal was approximately 1cm across (see Figure 3).

4 Achieving Frequency Doubling in a Homegrown Crystal

4.1 Aligning the KDP Crystal

4.1.1 Finding the Optical Axis

The KDP crystal is composed of a square crystal with pyramids at each end. The crystallographic c-axis is the longest direction of the crystal, which ends in pyramids at each side (see Figure 4) [8]. According to Fang and Lambropoulos (2002), the optical axis is identical to the c-axis of the KDP crystal [7].

4.1.2 Angle Calculation for Phase Matching

Using the phase matching theory in section 1.3 and the refractive indices given in Appendix A, I calculated the angle between the optical axis and the incident laser beam to achieve second harmonic generation. For the 1064nm Nd:YAG laser, I found the optical axis must be at a 41.1° angle to the incident beam, and for the 795nm titanium-sapphire laser, the optical axis must be at a 45.3° angle to the incident beam.

4.1.3 Experimental Setup

The laser is vertically polarized, so the c-axis must be placed horizontal. I laid the crystal on one of its four, flat rectangular faces on a rotatable stage. This allowed me to fine-tune the angle and reproducably find the point where I could see frequency doubling.

4.2 Results

4.2.1 Nd:YAG laser

I was not able to achieve frequency doubling with the Nd:YAG laser. I believe this is due to the low power of the laser. The laser is a continuous beam with 500mW power. According to Eimerl (1987), a minimum of 500mW of laser power is needed for frequency doubling to occur, so the Nd:YAG laser used in this experiment was on the very edge of usable lasers [9]. This combined with imperfections in the homegrown crystal made it impossible to see frequency doubling.

4.2.2 Titanium-sapphire Laser

Next I tried frequency doubling with the titanium-sapphire laser in Moungi Bawendi's Lab in the basement of building 18. This femtosecond-pulsed laser has a wavelength of 795nm and has 800mW power. The near infrared 795nm light appears as a faint red to the naked eye due to the high intensity of the light. After frequency doubling, the light is in the near ultraviolet (397.5nm) and visible as a dim blue-purple spot. To differentiate between the two beams, I wore safety glasses that blocked the infrared light, but not the ultraviolet light. It took about 10 minutes of careful angle adjustment to find a spot where I could see second harmonic generation. The results are shown in Figure 5.

5 Intensity of Second Harmonic in a KDP Crystal

Using an old, cracked commercial KDP crystal in the Modern Optics Lab, I was able to observe frequency doubling. It was easy to observe the output second harmonic beam because it was 532nm, green light, whereas the 1064nm beam from the laser was invisible to the naked eye. I used this commercial crystal to take intensity measurements of the frequency doubled light based on crystal angle. To do this, I mounted the crystal on a 2-axis rotational stage approximately 30cm from the laser. Since both the unchanged light and the frequency doubled light are output in the same direction, I placed an equilateral prism about 15cm behind the crystal to split the two beams. Finally, I placed an observation screen about a meter behind the prism. At this point, the two frequencies were about 1cm apart. See Appendix B for a picture of the actual experimental setup. The strong 1064nm output beam was blocked with a screen

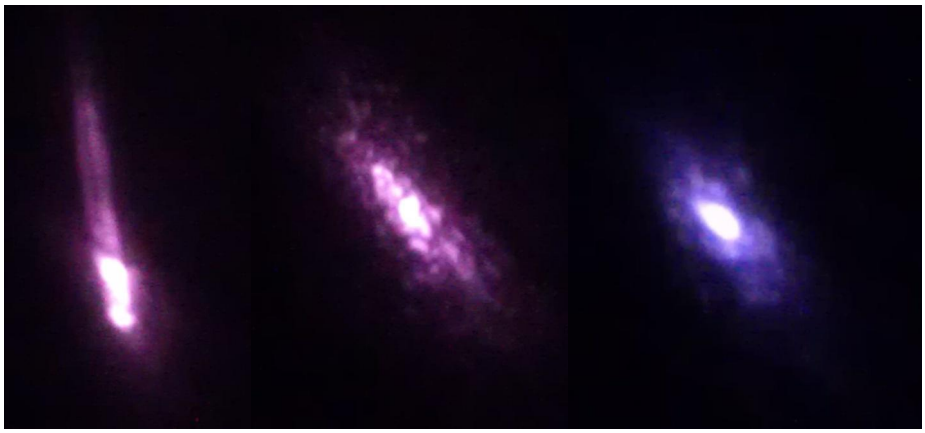

Figure 5: No frequency doubling (left), output beam when I first witnessed frequency doubling (middle), and output beam turning blue due to strong second harmonic generation (right).

before reaching the final observation screen, so that it would not interfere with intensity readings. A photodetector was used to measure the intensity of the frequency doubled beam. The results are plotted in Figure 6. I found that within an angle change of 0.5° I could no longer see the frequency doubled beam with the naked eye.

I also plotted the theoretical intensity for second harmonic generation. Both Δk and L can be plotted as a function of θ. In the case of the horizontal angle mismatch, the angle of the optical axis with the incident wave is changing, so both Δk and L are changing. The vertical mismatch case is different, because the only thing that should theoretically change is L. Changes in angle in the vertical direction are perpendicular to the optical axis, so the crystal is simply rotating in the plane of its two axes with the same refractive index n_o.

The theoretical intensity plots in Figure 6 vary extensively from the experimental intensity plots. There are several reasons why the experimental data does not match theory. Besides the assumptions made when deriving the equation for second harmonic generation intensity (see Section 2.5), I also had to make assumptions about the orientation of the crystal and its crystallographic axes. I assumed that the pre-cut crystal was cut so that the optical axis was at a 41.1° angle to the horizontal axis and that the vertical axis was perfectly perpedicular to the optical axis. I also assumed that when I placed the crystal in the 2-axis rotational stage and found the spot where I could see frequency doubling that the crystal was exactly normal to the incident beam.

Adjusting parameters in the theoretical intensity for the horizontal angle mismatch, I found that by changing the estimated crystal thickness to 0.5mm, the theoretical curve for horizontal angle mismatch widened and almost matched the experimental results. I had estimated the crystal to be 3mm, but with cracks and imperfections in the old crystal, perhaps 0.5mm is a better estimate of the

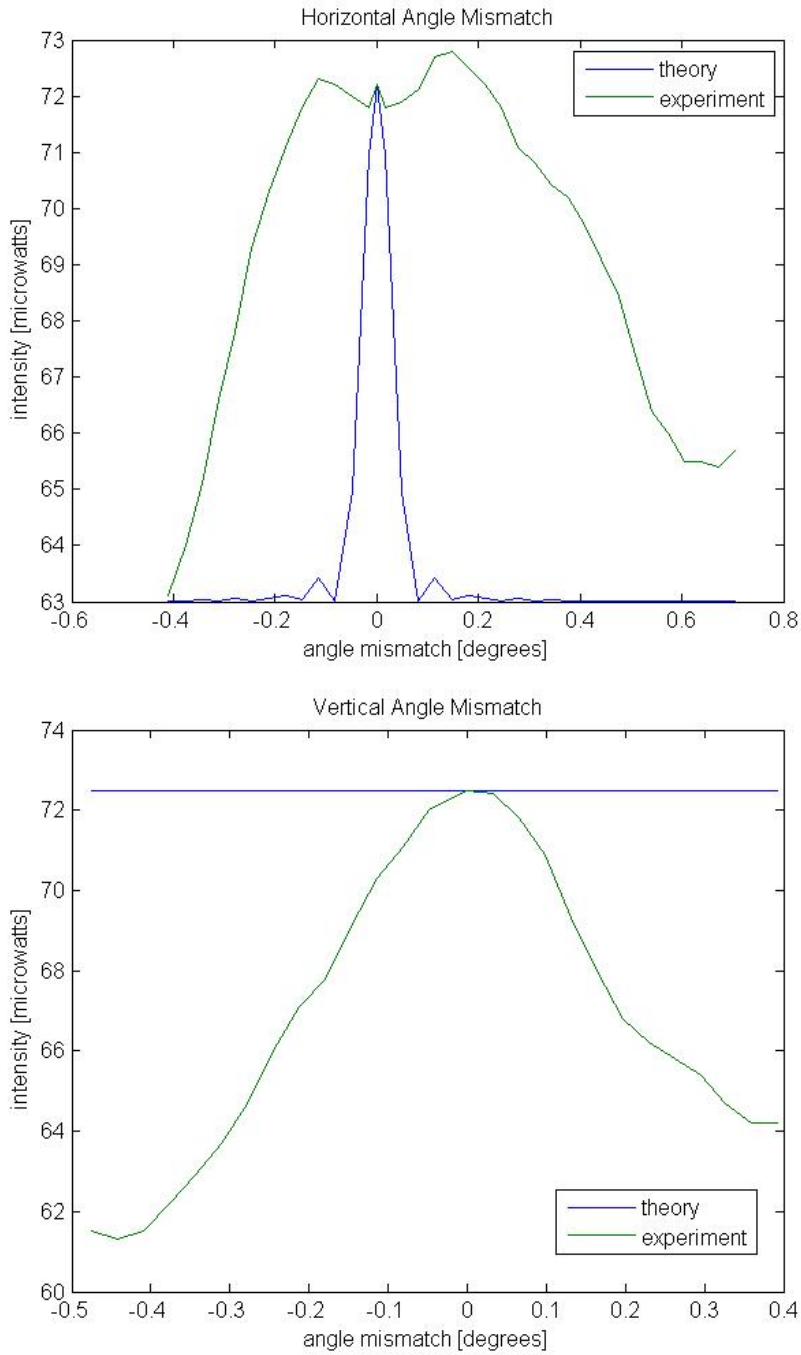

Figure 6: Comparison of experimental output intensity with theoretical output intensity as a function of angle.

thickness of crystal actually producing frequency generation. The broadened width of the experimental intensity curve in the horizontal angle mismatch could also be explained by the incident beam of light being not perfectly collimated, leading to a range of k-vectors (and thus angles) present for each measured angle.

I am not sure how to explain the grevious difference between theory and experiment in the case of the vertical mismatch, but I have several ideas. First of all, if the precut crystal's optical axis was not exactly horizontal, then changing the vertical angle would also change Δk and lead to a much tighter curve like in the horizontal mismatch case. I also hand-mounted the crystal to the center of the 2-axis rotation stage, so the crystal may have been vertically miscentered. If this were the case, then changing the vertical angle changed the location where the laser contacted the crystal and might have caused the laser to shine on imperfections or cracks in the crystal, greatly decreasing second harmonic output with changing angle.

6 Conclusion

This experiment showed that frequency doubling can be achieved in a homegrown KDP crystal with visible defects. I used the evaporation method to grow crystals over a period of days. It took three attempts to grow relatively clear crystals that would work for frequency doubling. Using a pulsed laser with 800mW power, I was able to see frequency doubling in my homegrown crystal. Due to low laser power, I was not able to successfully frequency double in my homegrown crystal in the 500mW Nd:YAG laser, but I was able to observe frequency doubling in a commercial KDP crystal. I used this commercial crystal to study the effect of angle on the output intensity of the frequency doubled beam. I found that by 0.5° angle change I could no longer see the frequency doubled beam with the naked eye.

In an effort to aid others working on similar experiments, I have created a blog online with the summaries of this report, which can be found at http://mit.edu/afritz/www/KDPcrystal.

References

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Appendix A: KDP Refractive Indicies

Calculated refractive indices at the harmonics of Nd : YAG

	4ω	3ω	2ω	1ω
KDP				
ord	1.560145	1.531114	1.512125	1.493807
ext	1.506028	1.485358	1.470396	1.459882

Figure 7: Data taken from Eimerl [9].

Indicies of refraction
(In 22°C air)

0.266µm	no=1.5599 ne=1.5105
0.3547µm	no=1.5318 ne=1.4864
0.532µm	no=1.5129 ne=1.4709
0.5893µm	no=1.5098 ne=1.4687
0.6328µm	no=1.5079 ne=1.4673
0.6943µm	no=1.5055 ne=1.4658
1.064µm	no=1.4944 ne=1.46035

Figure 8: Data taken from Cleveland Crystals, Inc. (http://www.clevelandcrystals.com).

Appendix B: Experimental Setup

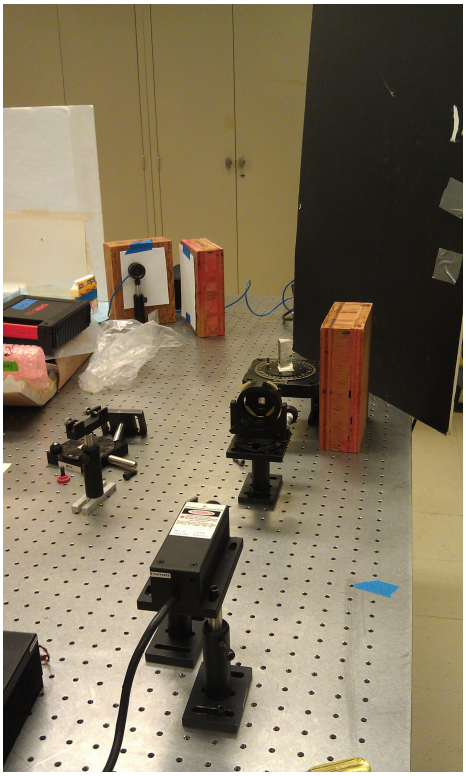

Figure 9: Experimental Setup for Measuring Output Intensity.

Appendix C: Matlab Code

```
nwo=1.493807;
nwe=1.459882
n2wo=1.512125;
n2we=1.470396;

a=-25:2:-1;
aa=0;
aaa=1:2:43;
a=[a, aa, aaa];
ia=[63.1 64 65.1 66.6 67.8 69.3 70.3 71.1 71.8 72.3 72.2 72.0 71.8 72.2 71.8
71.9 72.1 72.7 72.8 72.5 72.2 71.8 71.1 70.8 70.4 70.2 69.7 69.1 68.5 67.4 66.4
66 65.5 65.5 65.4 65.7]
anglea=atan(a.*.001./3.5);
degreesa=anglea*360/2/pi;
maxang=asin(sqrt((1/nwo^2-1/n2wo^2)/(1/n2we^2-1/n2wo^2)));
n2w=1./sqrt(1./n2we^2*((sin(anglea+maxang)).^2)+1./n2wo^2*((cos(anglea+maxang)
).^2));
deltak=4*pi/1064e-9*(nwo-n2w);
l=3e-3./cos(anglea);
I=9.2*sinc(deltak.*l/2).^2+63;
plot(degreesa,I,degreesa,ia)

figure
c=0:2:24;
b=-29:2:-3;
b=[b,c];
ib=[61.5 61.3 61.5 62.2 62.9 63.7 64.7 66 67.1 67.8 69.1 70.3 71.1 72 72.5 72.4
71.8 70.9 69.3 68 66.8 66.2 65.8 65.4 64.7 64.2 64.2]
angleb=atan(b.*.001./3.5);
degreesb=angleb*360/2/pi;
deltak=4*pi/1064e-9*(10^-9);
l=3e-3./cos(angleb);
I=11*sinc(deltak.*l/2).^2+61.5;
plot(degreesb,I,degreesb,ib)
```