About Scherrer Equation

0. Problem Proposed

In this article, the basic derivation of Scherrer equation and some explanation will be given. This summary is based on the online tutorial given in Ref-1. According to Bragg's law:

$n\lambda=2d\sin\theta$

If the imcoming angle θ satisfies the Bragg's equation regarding the given wavelength, the diffraction maximum could then be observed. And mathematically that means a vertical spike at the angle satisfying Bragg's equation in the Int. VS 2θ diagram. Basically, the diffraction maximum comes from the $2n\pi$ phase difference between the scattered beams. If the phase difference is away from $2n\pi$, the intensity of the scattered beam is less than the diffraction maximum (which corresponds to the $2n\pi$ phase difference). Therefore, if we have infinite lattice, the tiny phase difference will lead to infinite difference as the angle goes away from the Bragg angle. So for infinite lattice, the diffraction maximum is just a spike which means the scattering intensity is infinite for diffraction maximum as compared to other situations. However, the infinite lattice is ideal while the real lattice is with finite size. Therefore for real lattice, the difference between diffraction maximum and other situations is not infinite, which means we don't have a diffraction spike, instead we have a peak with certain width. Then natually, it is easy to understand that the width of the diffraction peak is actually determined by the size of lattice. Or the other way round, we can determine the crystallization size based on the width of the diffraction peak. And this is just where the Scherrer equation comes to help.

1. Derivation-1

Starting from the Bragg's law:

$n\lambda=2d\sin\theta$

By setting 'n=1', and we should have 'd' corresponding to imagined lattice planes lying in between the real ones, then the Bragg's equation becomes the commonly used form:

$\lambda=2d\sin\theta$

where 'd' may correspond to either the real or imagined lattice planes. Assuming the crystal size is *t*, corresponding to m lattice planes (thus t=md, where d is the lattice spacing), we have:

$$m\lambda = 2\,md\sin\theta = 2\,t\sin\theta \tag{1.1}$$

By differentiating (1.1), we then have (keep in mind that λ is constant):

$$0 = 2\,\Delta t\sin\theta + 2\,t\cos\theta\Delta\theta \tag{1.2}$$

If only considering the absolute value of $\Delta\theta$, we have:

$$t = \left| \frac{\Delta t\sin\theta}{\cos\theta\Delta\theta} \right| \tag{1.3}$$

Furthermore, we know that the unit of lattice size changing is just the lattice spacing so we have $\Delta t=d$, also considering the Bragg's law, (1.3) then becomes:

$$t=\frac{\lambda}{2\,cos\theta\Delta\theta} \tag{1.4}$$

Let $B=2\Delta\theta$, (1.4) then becomes:

$$t=\frac{\lambda}{Bcos\theta} \tag{1.5}$$

This is just the Scherrer equation, where B is the full width at half maximum in 2θ space. For further explanation, refer to part-4 of this article. Also for further understanding about the finite lattice size effect, both from the physical and mathematical point of view, refer to Part-3.

2. Derivation-2

In part-1, it was given the derivation of Scherrer equation. And here in this section, another derivation method is given. Assuming the center of Bragg peak is $\boldsymbol{\theta_B}$, then naturally we have:

$$\lambda = 2\,dsin\theta_B \tag{1.6}$$

Again we have:

$$\mathrm{m}\lambda = 2\,\mathrm{md}sin\theta_B = 2\,tsin\theta_B \tag{1.7}$$

Then we assume the scattering intensity goes to zero when the incoming angle becomes $\theta_1$or $\theta_2$on the two sides of the peak center θ_B. Mathematically we have:

$$2\,tsin\theta_1 = (m+1)\,\lambda \tag{1.8}$$

$$2\,tsin\theta_2 = (m-1)\,\lambda \tag{1.9}$$

For more explanation about (1.8) and (1.9), refer to Part-4. Here we combine (1.8) and (1.9):

$$t(sin\theta_1 - sin\theta_2) = \lambda \tag{1.10}$$

Furthermore,

$$2\,tcos\frac{\theta_1+\theta_2}{2}\,sin\frac{\theta_1-\theta_2}{2} = \lambda \tag{1.11}$$

Assuming the diffraction peak is narrow, we could have: $\theta_1+\theta_2 \sim \theta_B$ and $(\theta_1-\theta_2)/2 \sim 0$, then we have :

$$sin\frac{\theta_1-\theta_2}{2} \sim \frac{\theta_1-\theta_2}{2} \tag{1.12}$$

$$2\,t\,\frac{\theta_1-\theta_2}{2}\,cos\theta_B = \lambda \tag{1.13}$$

$$t=\frac{\lambda}{Bcos\theta_B} \tag{1.14}$$

where $B=\theta_1-\theta_2$. In part-1, we assign $B=2\Delta\theta$, which is actually the same as $B=\theta_1-\theta_2$ as given here.

3. Some Explanation

3.1 Physicsally

Now we can calculate the crystallinity based on the width of the Bragg diffraction peak. However it worths pointing out the physics behind the scene. Actually for the physical understanding for Scherre equation, it has already been discussed at the begining. Basically, what diffraction concerns about is just the phase difference between the scattered beam. If each two of the scattered beam is with the phase difference of $2n\pi$ (in wavelength space, this correspond to $n\lambda$), then we will definitely have the diffraction maximum. The thing is if the angle goes away from the Bragg angle, what is the difference between the diffraction maximum and those other situations (when angle is away from the diffraction maximum angle)? Of course the corresdponding scattering intensity will turn to become small. Imagine we have a tiny shift of angle from the peak center, then for infinite crystal where we have infinite number of lattice planes, the reduction of the scattering intensity due to the tiny shift of the angle (which then means the tiny shift of the phase difference from $2n\pi$) will accumulate to infinity. The result is that the intensity of the Bragg peak is infinite compared to those for other situations. While for the finite crystal size, the intensity reduction effect due to the phase difference does not accumulate to infinity, which then gives us a diffraction peak with finite width.

3.2 Mathematically

From the perspective of mathematics, the diffraction pattern is the Fourier transform of the lattice. Then it is easy to understand that if we have an infinite lattice, that is equivalent to say we have an infinite signal in real space for which we need to do the Fourier transformation. The result is certainly a spike signal in the reciprocal space. If we are doing Fourier transform for a signal with finite width in real space, the result is equivalent to do Fourier transform a infinite signal multiplied by a window function. In reciprocal space, the result is the δ function convoluted by a peak with certain width - the result is just a peak with certain width. For more details, refer to the appendix.

4. More Notes To Take Down

4.1 About ‘B’ - FWHM - In Scherrer Equation

From the definition for $B = \theta_1 - \theta_2$, we know that in θ space, B is the ‘distance’ from one end of the diffraction peak to another. However, commonly we will use the $2\,\theta$ space, where the ‘distance’ between the two ends is now actually $2(\theta_1 - \theta_2)$. Therefore in 2θ space, B should be half of the ‘distance’ between the two ends, i.e. $\frac{1}{2}\,2\,(\theta_1 - \theta_2)$. Usually we will use the full width at half maximum to represent the value of $\frac{1}{2}\,2\,(\theta_1 - \theta_2)$, i.e. B~FWHM. However from the discussion in the context, we can see that as a matter of fact, FWHM is actually not the exact value for $\frac{1}{2}\,2\,(\theta_1 - \theta_2)$ but just an approximation.

Moreover, from (1.2), it can be inferred that the broadening of the diffraction peak is actually considered as the tiny shift of the main diffraction peak. In another word, the broadening of the diffraction is taken as some kind of uncertainty - there could exist some shift of the diffraction peal position. Then from this perspective, we may have the question - what is the reason contributing to the tiny shift (or, the uncertainty) of the diffraction peak? Physically, we could imagine a tiny shrink or expansioon of the lattice we are looking at. If we have a shrink of the lattice spacing, according to the Bragg’s law, we may have the diffraction peak shift to the left by a bit. And if the lattice is expanding, then we may have the peak shift to the right by a bit accordingly. Then how do we determine to what extent that the lattice spacing can shrink or expand? While, we need to consider the accumulation of the lattice spacing changing, keeping in mind that we have the restriction condition that when the lattice is considered a whole then the changing unit of the whole lattice size is just the lattice spacing. That’s to say, if we have a tiny changing for each single lattice spacing, then the accumulation of all the lattice spacing changing for the whole lattice in question should be just a single lattice spacing. And this is just the reason why we have (1.8) and (1.9).

4.2 Look At The Limitation of Scherrer Equation

As a matte of fact, there are indeed some limitations for the application of the Scherrer equation to determine the crystallization size. From the discussion in Part-4.1, we know that the representation of $\frac{1}{2}\,2\,(\theta_1 - \theta_2)$ using the FWHM is itself an serious approximation. Moreover, when the diffraction peaks is too broad, the Scherrer equation again encounters with certain problem. During the derivation process, the following approximation was used as one of the key steps:

$$sin\,\frac{\theta_1 - \theta_2}{2} \sim \frac{\theta_1 - \theta_2}{2} \tag{1.15}$$

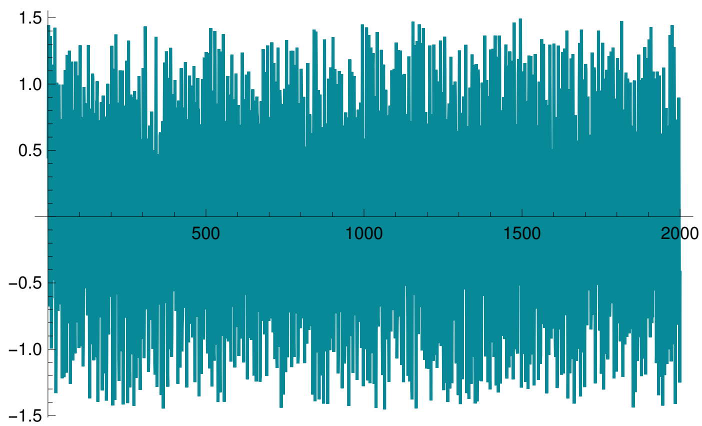
As we know if $\frac{\theta_1 - \theta_2}{2}$becomes significantly large, the above approximation does not hold any more. Therefore the Scherrer equation in such case may not give the correct description of the lattice crystallization size. On the other hand, if the diffraction peak is quite sharp, which means we may have quite large crystallization size, there will also be some problems in the application of the Scherrer equation. That’s because in practical situation, it cannot be avoided that we should have the peak broadening due to the measurement facility (e.g. the uncertainty or vibration of the wavelength of the beam used for the measurement). And if the diffraction peak itself is quite narrow, that makes it difficult to extract the real peak broadening purely due to the finite lattice size!

A

Fourier Transform For Finite Signal

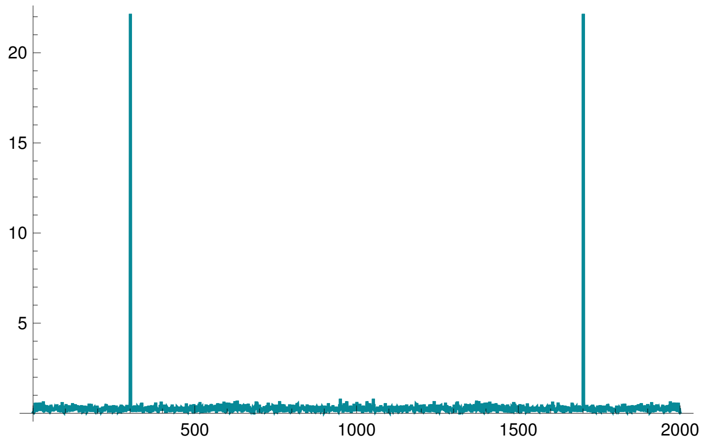
In this appendix, it will be given several examples of discrete Fourier transform to show directly the influence of the width of the signal in real space on the ‘diffraction peak’ width in the reciprocal space. The first example is from the *Mathematica* online documents (Click Me to show the original web source, if the link does not work, copy the address to browser: http://reference.wolfram.com/language/tutorial/FourierTransforms.html):

```
data = Table[N[Sin[30 × 2 Pi n / 200] + (RandomReal[] - 1 / 2)], {n, 2000}];
ListLinePlot[data]
```



The above signal ‘data’ in real space is with the width of 500, and from the definition of the signal it can be seen that the signal is just a periodic signal plus some given noise (by ‘RandomReal’ function). After Fourier transform, the signal shown in reciprocal space will give direct information about the property of the given signal - that’s just why we need Fourier transform everywhere for signal analysis. The following is the Fourier transform (of course, discrete) of the above signal:

```
ListLinePlot[Abs[Fourier[data]], PlotRange → All]
```

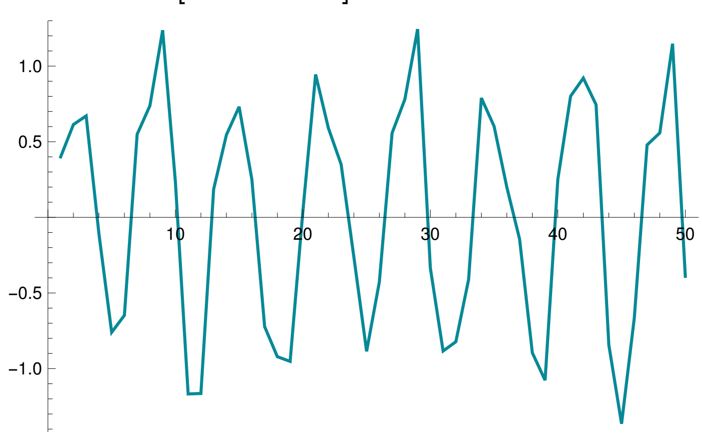


The ‘Abs’ function calculates the modulus of given input - remember Fourier transform gives the output of complex number and in this case we are concerned about the modulus of it. As shown in the above figure, the Fourier transform of the ‘noisy’ signal in real space gives us ‘spike’ in reciprocal space, which means we have single frequency component. It does make sense since indeed we have single frequency in the original definition of the signal in real space. Here it needs some explanation about why we have two spikes in the Fourier transform before going on to discuss the influence of the width of the signal in real space. First of all, the formulization of discrete Fourier transform algorithm uses the same grid, i.e. the unit and width of the signal in real and reciprocal space is identical to each other. Here it is necessary to recall the ‘symmetric’ property of the Fourier transform - the Fourier transform of a discrete periodic signal (for finite signal, the width is just the periodicity) gives also a discrete periodic signal (discrete <-> periodic & periodci <-> discrete). Therefore it is straightforward to figure out why the formulization of discrete Fourier transform uses the same grid for signal in real and reciprocal space. Actually, it is a must result required by mathematics behind the scene. Also we should recall the so-called negative frequency which was introduced when deriving the formulization of Fourier transform using its complex form instead of the ‘cos’ and ‘sin’ terms. Therefore in the full frequency space, we should also include the negative part. However, according to the basic Fourier transform theory, the modulus of the signal in the full frequency space is symmetric along the y-axis, i.e. the negative frequency gives the identical result with that given by its corresponding opposite number in the positive side. Then we could see how the second spike in the above figure comes, which is actually the requirement of both even symmetry and periodicity of the signal in reciprocal space.

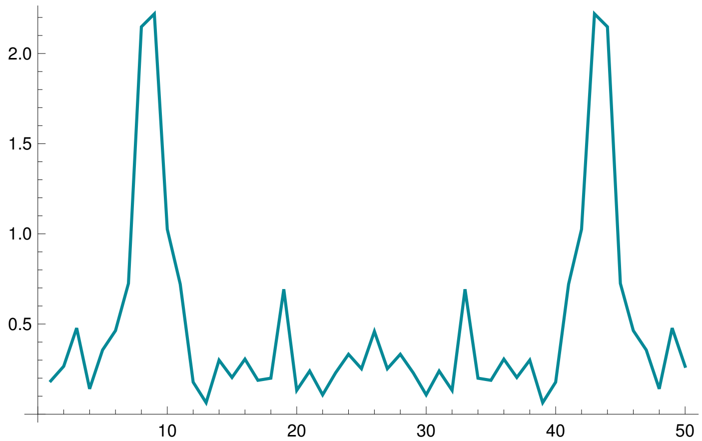
Now it’s time to have a look at the influence of the signal width in real space on the Fourier transform result shown in the reciprocal space:

```
data`narrow = Table[N[Sin[30 × 2 Pi n / 200] + (RandomReal[] - 1 / 2)], {n, 50}];
```

```
ListLinePlot[data`narrow]
```



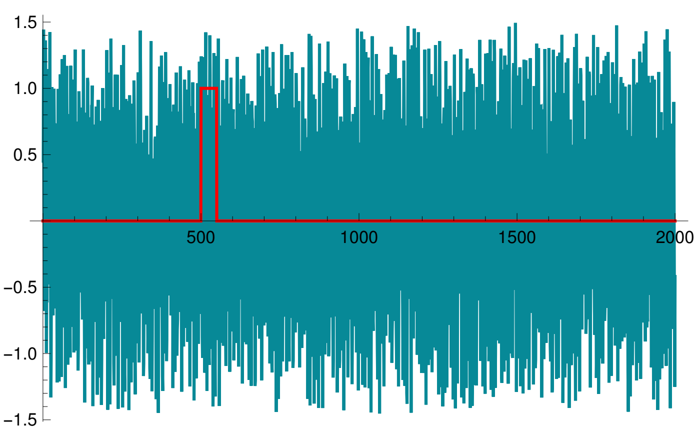
```
ListLinePlot[Abs[Fourier[data`narrow]], PlotRange → All]
```



We can now see that by reducing the width of the signal in real space, we indeed obtain a broader ‘diffration peak’ in the reciprocal space. Here there may be a question about the scale of the above two figures in reciprocal space - the first one is [0,2000] and the second one is [0,50]. Can we directly compare the width of them? Shoudn’t we plot the second one in the scale of [0,2000] and then compare them? The answer is no, we don’t need to do the rescaling. For the first figure, the large scale is only because we have more broad data in real space therefore the resolution is higher than the bottom signal (where we have a narrow signal in real space - [0,50] as compared to [0,2000]). And when the Fourier transform is carried out, it assigns each discrete point in the reciprocal space an integer value. Therefore we can say, the integet indexing itself brings different scaling of Fourier transform signal in reciprocal space. Actually we can directly divide the first and second signal in reciprocal space with 2000 and 50 respectively to obtain the unified scaling for comparison. But that does nothing to the shape of the plotting and the real width of the signal in reciprocal space.

Now we look at the influence of signal width from another perspective. Actually, when we transform from infinite signal to signal with finite width, it is equivalent to time the infinite signal with a window function. For the Fourier transform, the result for the composite signal is the convolution of the Fourier transform of the ‘infinite’ signal with that of the window function:

```
Show[ListLinePlot[data], Plot[DirichletWindow[(x - 525) / 50], {x, 0, 2000}, PlotStyle → Red]]
```



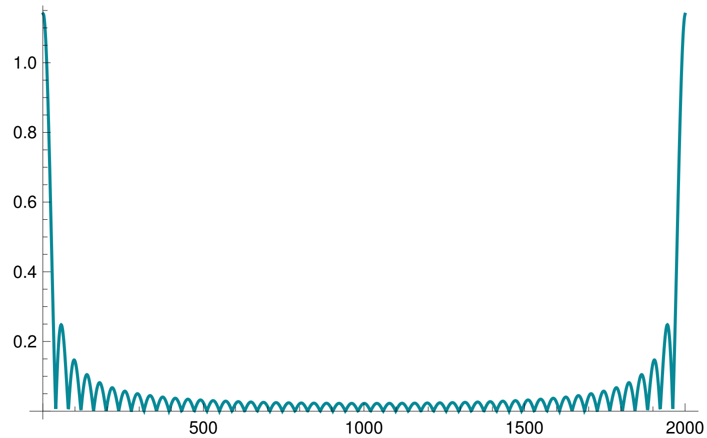
When multiplying the two signals shown in the above figure, we will obtain exactly the same signal as given by the second example shown above. But now we change the route to do the Fourier transform through convolution. First is the Fourier transform of the ‘infinite’ signal:

```
infinite`fourier = Table[{i, Abs[Fourier[data]][[i]]}, {i, 1, Length[Abs[Fourier[data]]]}];
```

Then is the Fourier transform of the window function:

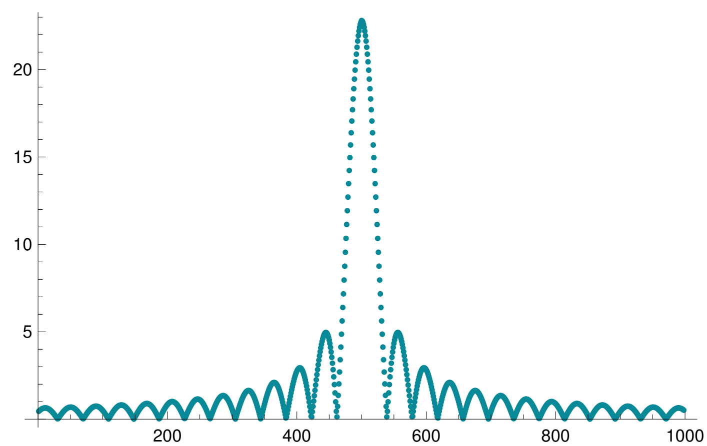
```
window`data = Table[DirichletWindow[(n - 525) / 50], {n, 2000}];

window`fourier =
  Table[{i, Abs[Fourier[window`data]][[i]]}, {i, 1, Length[Abs[Fourier[window`data]]]}];
```

```
ListLinePlot[window`fourier, PlotRange → All]
```

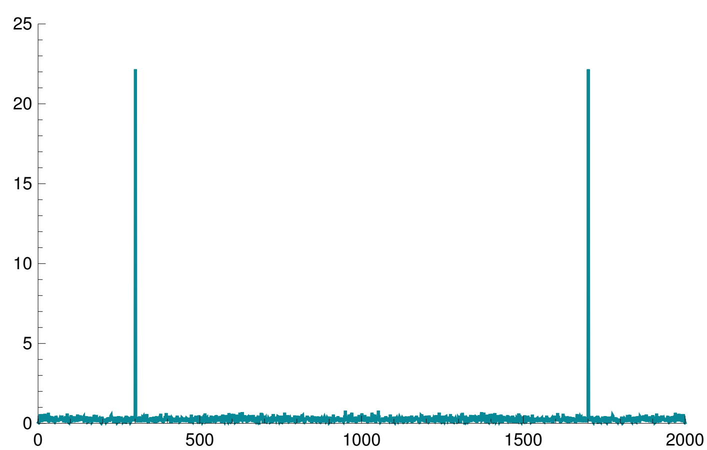


Transform to the full frequency space with negative frequency:

```
window`fourier`full = Table[If[i < 500, 20 * Abs[Fourier[window`data]][[i + 1500]],
    20 * Abs[Fourier[window`data]][[i - 499]]], {i, 1, 998}];
ListPlot[window`fourier`full, PlotRange → All]
```

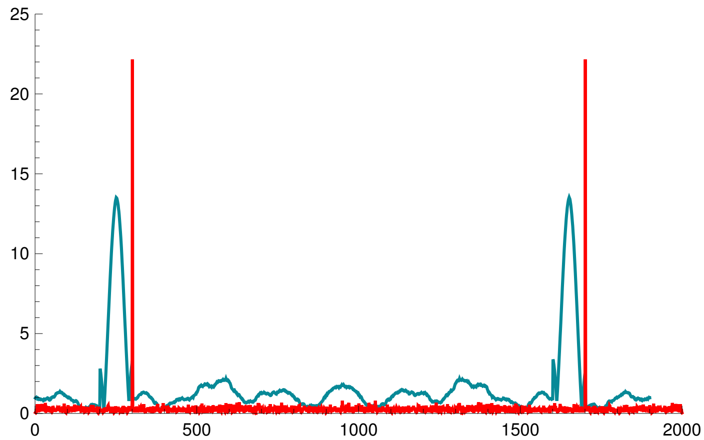


```
ListLinePlot[Abs[Fourier[data]], PlotRange → {{0, 2000}, {0, 25}}]
```



```
window`convolution =
  ListConvolve[window`fourier`full[[450 ;; 550]] / 40, Abs[Fourier[data]]];
```

```
Show[ListLinePlot[window`convolution - 6, PlotRange → {{0, 2000}, {0, 25}}],
 ListLinePlot[Abs[Fourier[data]], PlotRange → {{0, 2000}, {0, 25}}, PlotStyle → Red]]
```



Here the peak profile broadening is obvious by comparing the plotting before and after the convolution with the Fourier transform of window function. However it is obvious that there is a shift of the peak profile which is not expected. This is due to the window function we select here in this context is the rectangle window function, which is of course not a perfect (or even a correct one) window function. However, here we are only focusing on the broadening effect, qualitatively.

References

A. Miguel Santiago, "Introduction to X-ray Diffractiometer" Online Tutorial (If the link does not work, copy the following address: https://1drv.ms/b/s!AlZpbyasn9jtgYd-UdZ-Knw4IB1ssg)