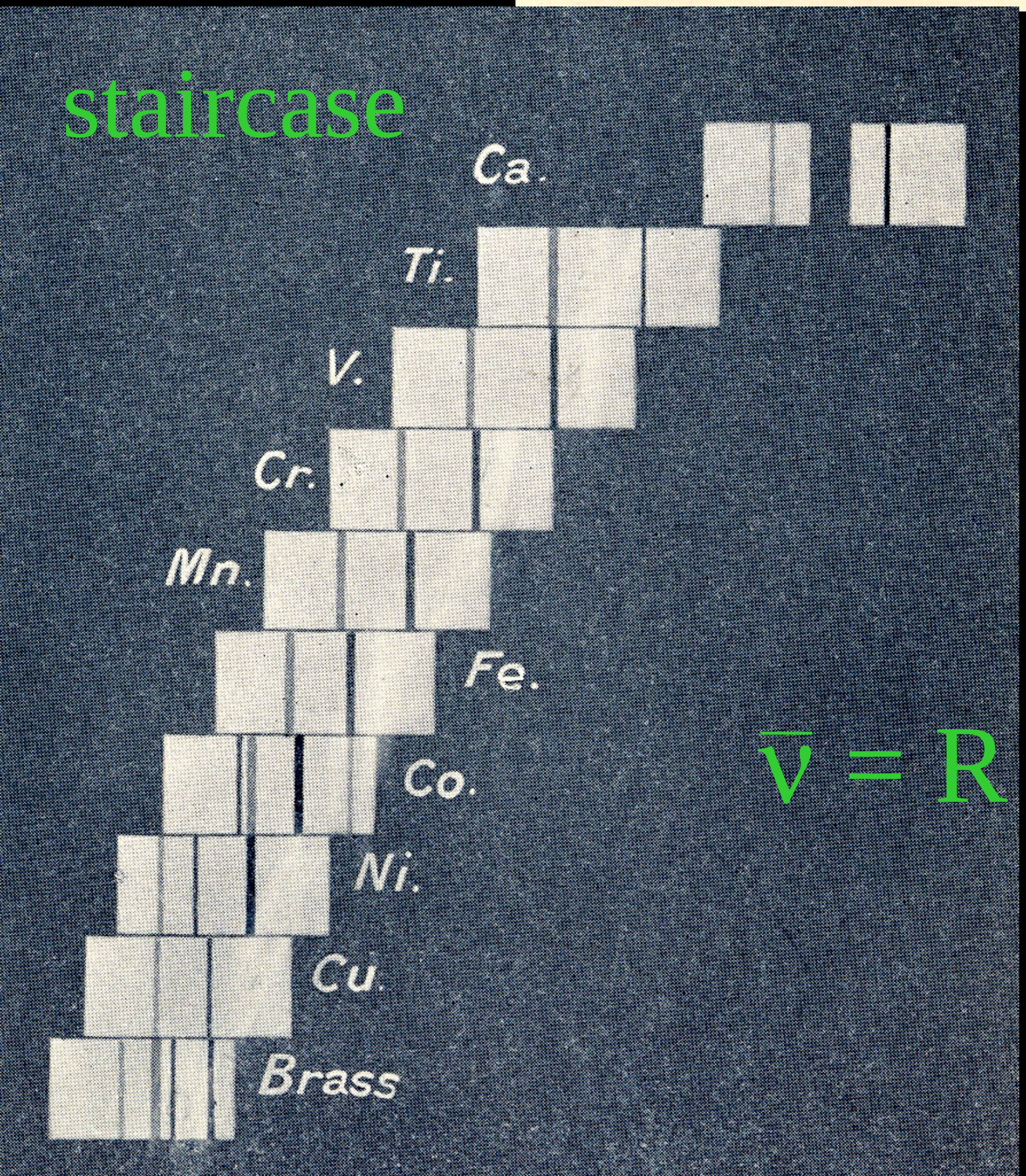
Welcome to 3.091

Lecture 18

October 21, 2009

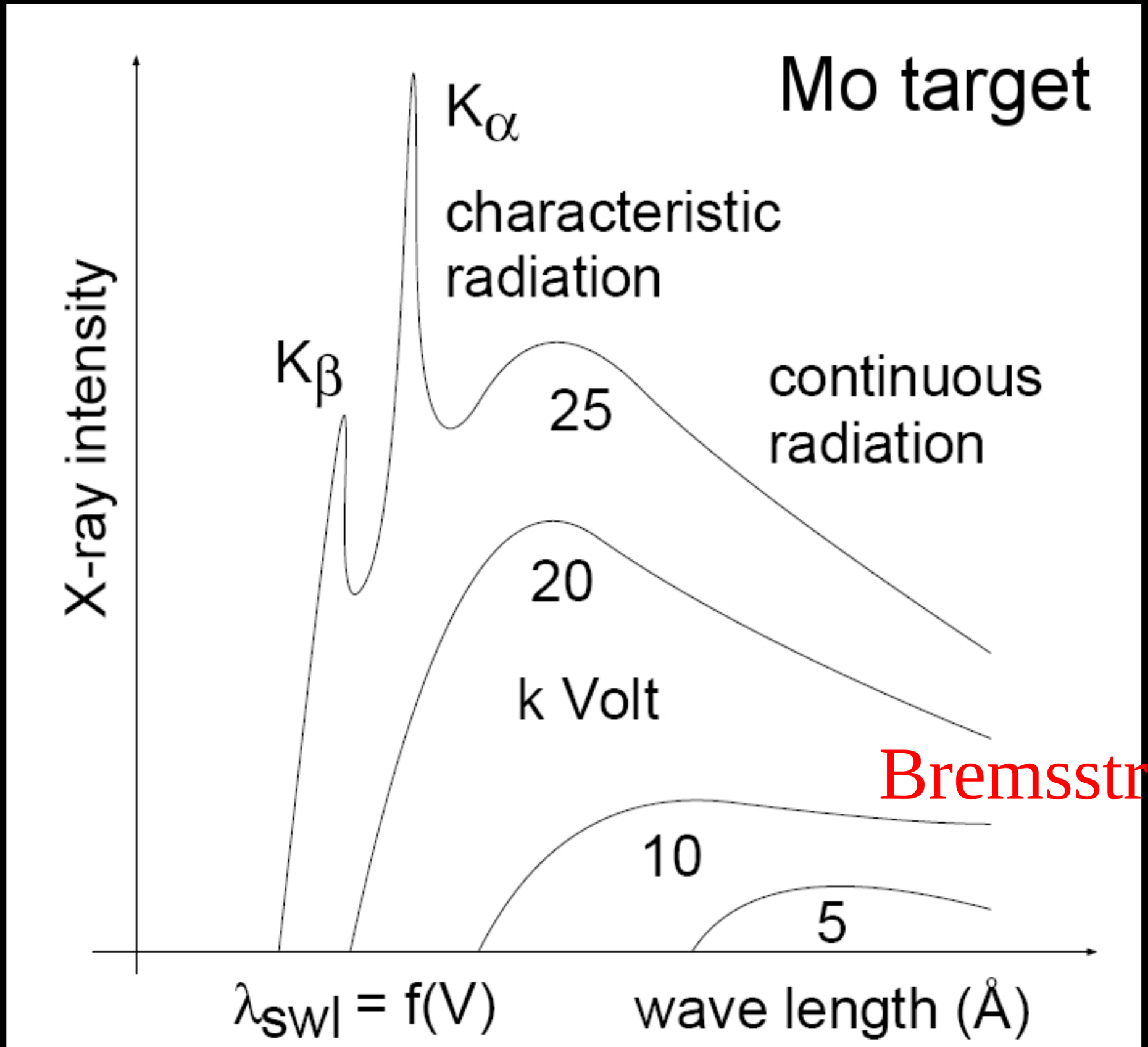
X-Ray Diffraction Techniques

staircase



Moseley's Law

$$\bar{\nu} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)\left(Z\text{-}\sigma\right)^2$$



Bremsstrahlung

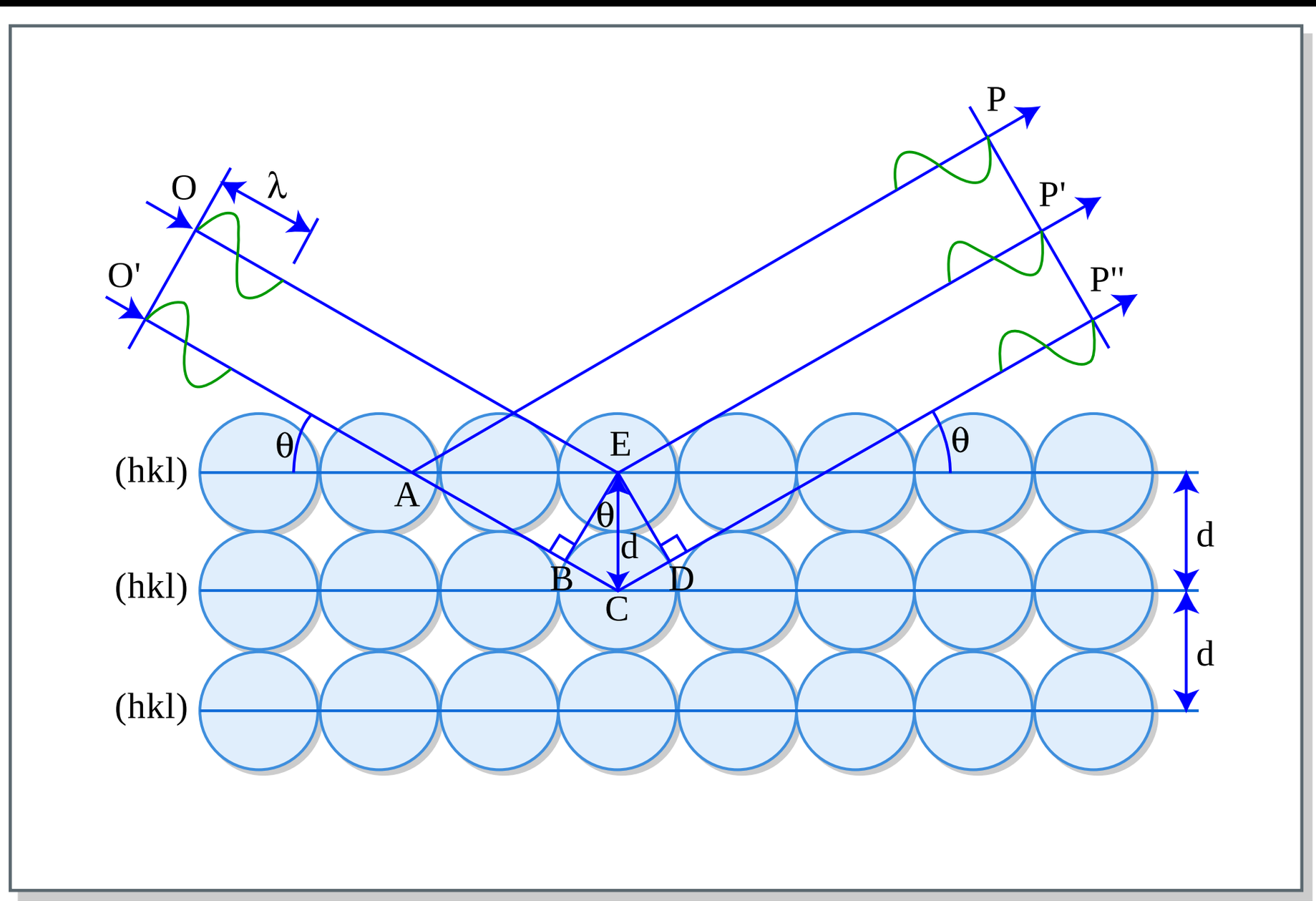
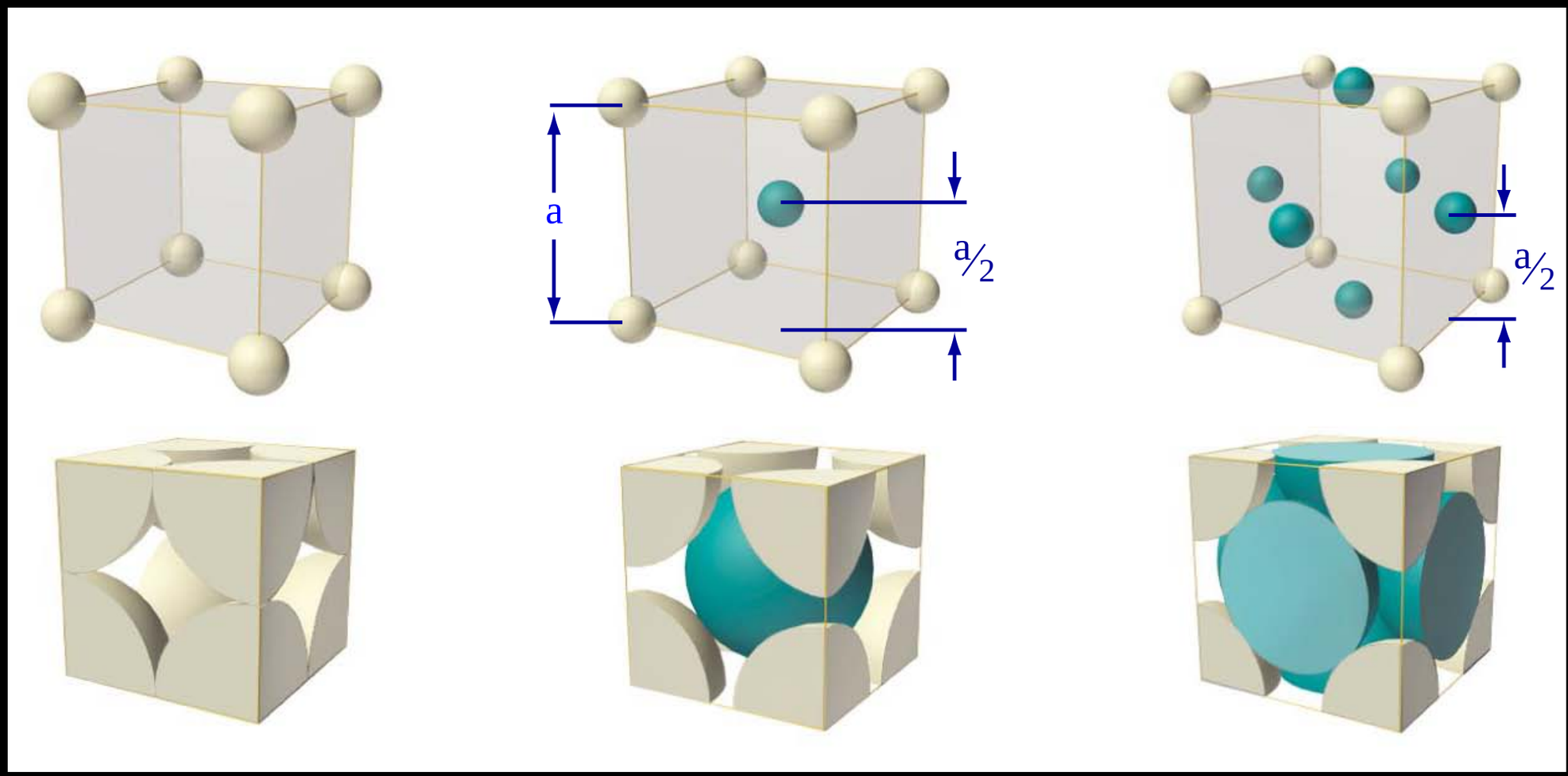


Image by MIT OpenCourseWare.



Averill, B., and P. Eldredge. *Chemistry: Principles, Patterns, and Applications*. Flat World Knowledge, 2011. ISBN: 9781453331224.

Selection Rules for Reflection in Cubic Crystals

(*hkl*)	$h^2+k^2+l^2$	SC	BCC	FCC
100	1	✓	✖	✖
110	2	✓	✓	✖
111	3	✓	✖	✓
200	4	✓	✓	✓
210	5	✓	✖	✖
211	6	✓	✓	✖
220	8	✓	✓	✓
300	9	✓	✖	✖
310	10	✓	✓	✖
311	11	✓	✖	✓
222	12	✓	✓	✓
320	13	✓	✖	✖
321	14	✓	✓	✖
400	16	✓	✓	✓

all

h+k+l

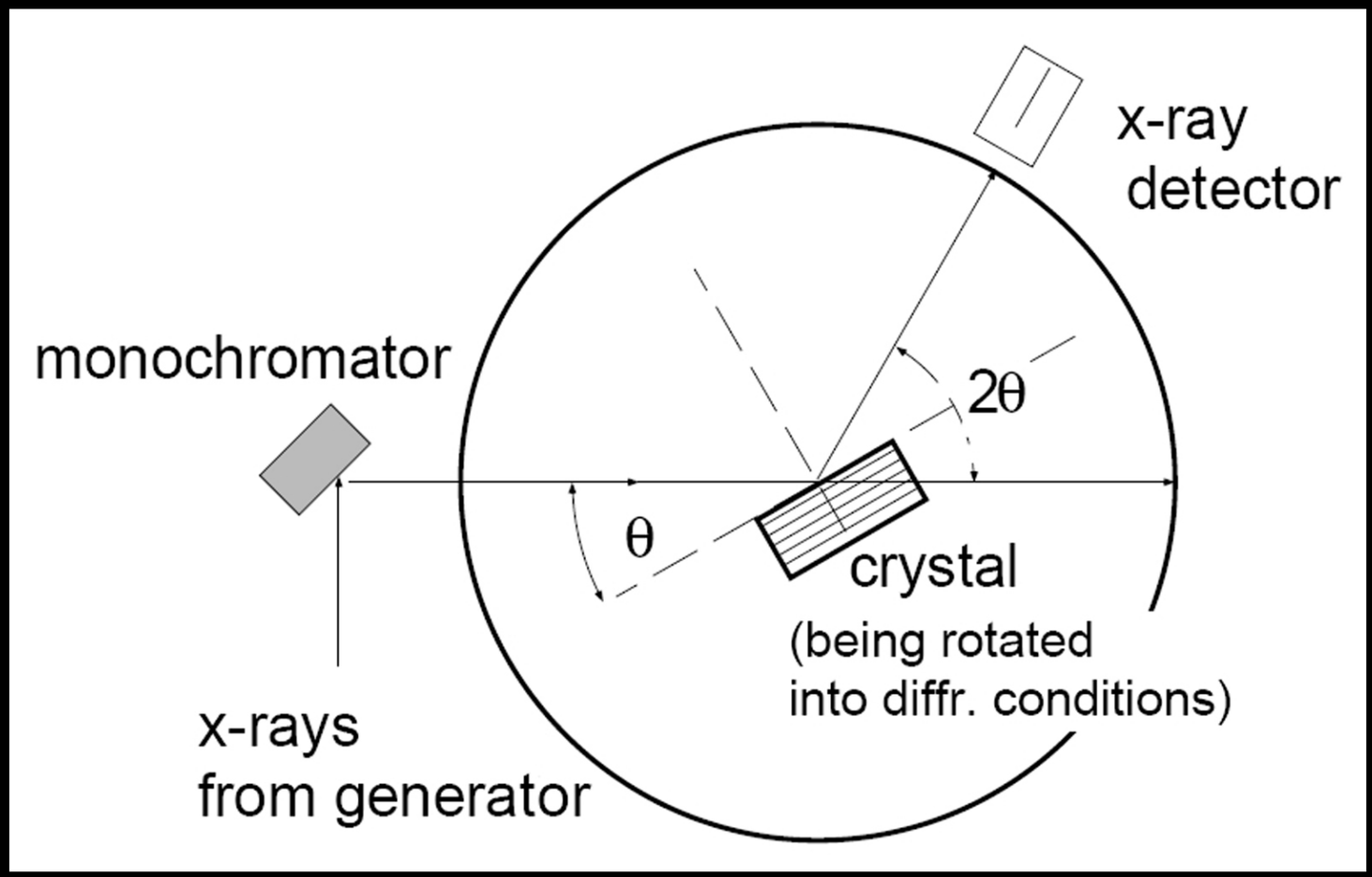
h+k+l

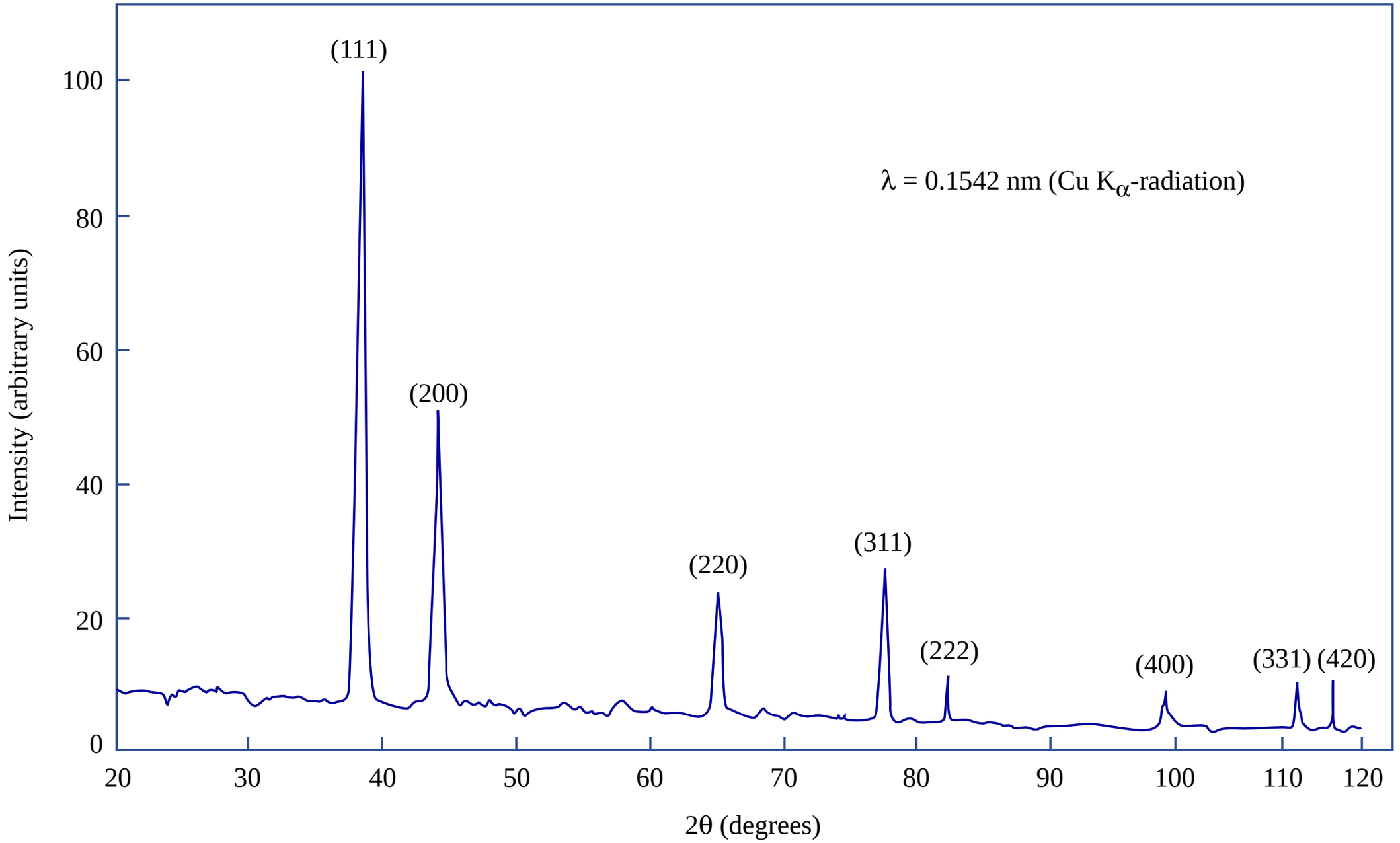
all even

or all odd

unmixed

diffractometry





Cu target, $\lambda_{K\alpha} = 1.5418$ Å

2θ
44.48
51.83
76.35
92.90
98.40
121.87
144.54
155.51

Sadoway's Five-step Program for Determining Crystal Structure

Step 1 Start with 2θ values and generate a set of $\sin^2\theta$ values.

Cu target, $\lambda_{K\alpha} = 1.5418$ Å

2θ	$\sin^2\theta$
44.48	0.143
51.83	0.191
76.35	0.382
92.90	0.525
98.40	0.573
121.87	0.764
144.54	0.907
155.51	0.955

Sadoway's Five-step Program for Determining Crystal Structure

Step 1 Start with 2θ values and generate a set of $\sin^2\theta$ values.

Step 2 Normalize the $\sin^2\theta$ values by generating $\sin^2\theta_n / \sin^2\theta_1$.

Cu target, $\lambda_{K\alpha} = 1.5418$ Å

2θ	$\sin^2\theta$	normalized
44.48	0.143	1.00
51.83	0.191	1.34
76.35	0.382	2.67
92.90	0.525	3.67
98.40	0.573	4.01
121.87	0.764	5.34
144.54	0.907	6.34
155.51	0.955	6.68

Sadoway's Five-step Program for Determining Crystal Structure

Step 1 Start with 2θ values and generate a set of $\sin^2\theta$ values.

Step 2 Normalize the $\sin^2\theta$ values by generating $\sin^2\theta_n / \sin^2\theta_1$.

Step 3 Clear fractions from "normalized" column.

Cu target, $\lambda_{K\alpha} = 1.5418$ Å

2θ	$\sin^2\theta$	normalized	clear fractions
44.48	0.143	1.00	3
51.83	0.191	1.34	4
76.35	0.382	2.67	8
92.90	0.525	3.67	11
98.40	0.573	4.01	12
121.87	0.764	5.34	16
144.54	0.907	6.34	19
155.51	0.955	6.68	20

Sadoway's Five-step Program for Determining Crystal Structure

Step 1 Start with 2θ values and generate a set of $\sin^2\theta$ values.

Step 2 Normalize the $\sin^2\theta$ values by generating $\sin^2\theta_n / \sin^2\theta_1$.

Step 3 Clear fractions from "normalized" column.

Step 4 Speculate on the hkl values that, if expressed as $h^2+k^2+l^2$, would generate the sequence of the "clear fractions" column.

Cu target, $\lambda_{K\alpha} = 1.5418$ Å

2θ	$\sin^2\theta$	normalized	clear fractions	(hkl)?
44.48	0.143	1.00	3	111
51.83	0.191	1.34	4	200
76.35	0.382	2.67	8	220
92.90	0.525	3.67	11	311
98.40	0.573	4.01	12	222
121.87	0.764	5.34	16	400
144.54	0.907	6.34	19	331
155.51	0.955	6.68	20	420

Sadoway's Five-step Program for Determining Crystal Structure

Step 1 Start with 2θ values and generate a set of $\sin^2\theta$ values.

Step 2 Normalize the $\sin^2\theta$ values by generating $\sin^2\theta_n / \sin^2\theta_1$.

Step 3 Clear fractions from "normalized" column.

Step 4 Speculate on the *hkl* values that, if expressed as $h^2+k^2+l^2$, would generate the sequence of the "clear fractions" column.

Step 5 Compute for each θ the value of $\sin^2\theta / (h^2+k^2+l^2)$ on the basis of the assumed *hkl* values. If each entry in this column is identical, then the entire process is validated.

Cu target, $\lambda_{K\alpha} = 1.5418$ Å

2θ	$\sin^2\theta$	normalized	clear	(hkl)?	$\frac{\sin^2\theta}{h^2+k^2+l^2}$
		fractions			
44.48	0.143	1.00	3	111	0.0477
51.83	0.191	1.34	4	200	0.0478
76.35	0.382	2.67	8	220	0.0478
92.90	0.525	3.67	11	311	0.0477
98.40	0.573	4.01	12	222	0.0478
121.87	0.764	5.34	16	400	0.0477
144.54	0.907	6.34	19	331	0.0477
155.51	0.955	6.68	20	420	0.0478

Selection Rules for Reflection in Cubic Crystals

(*hkl*)	$h^2+k^2+l^2$	SC	BCC	FCC
100	1	✓	✖	✖
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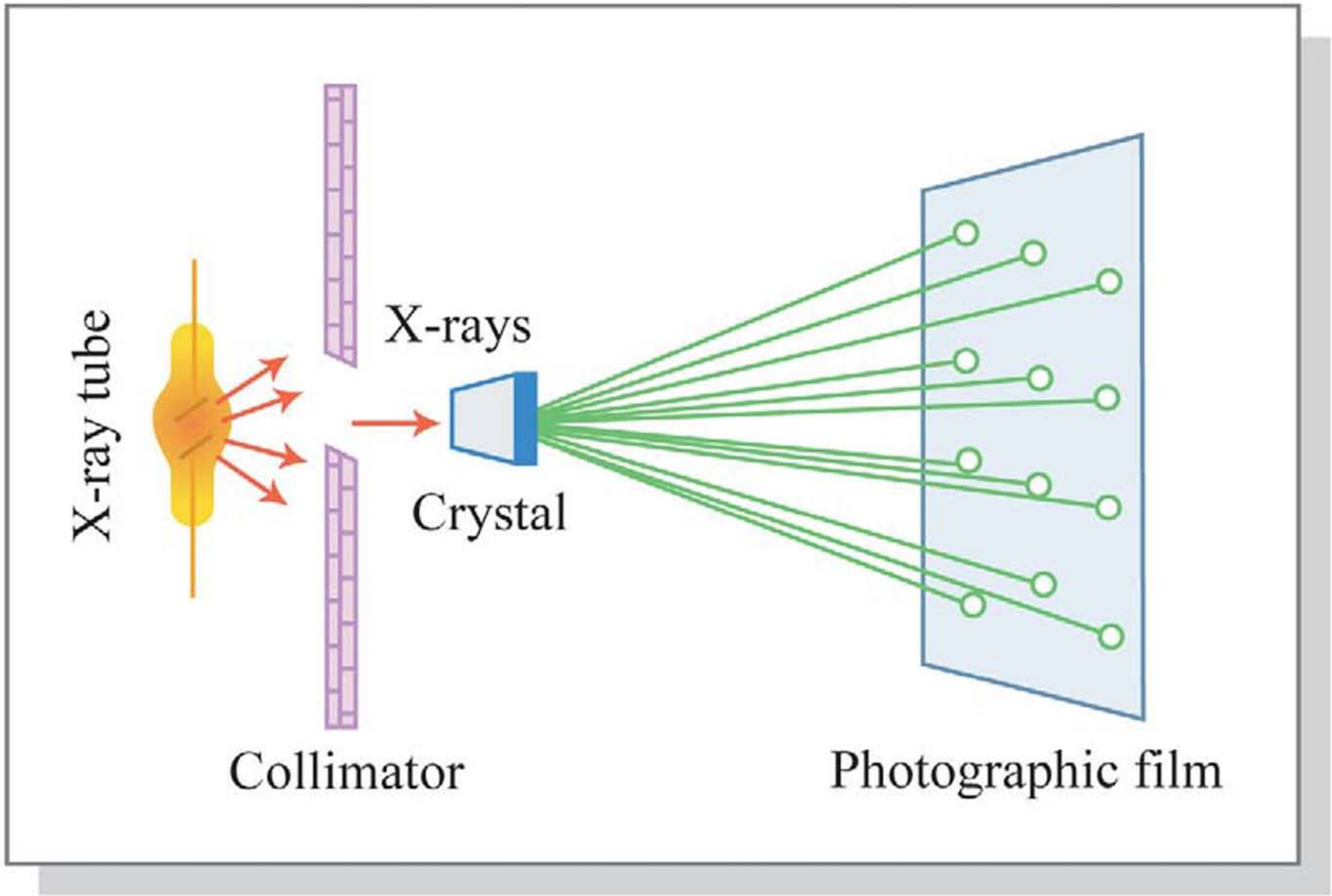
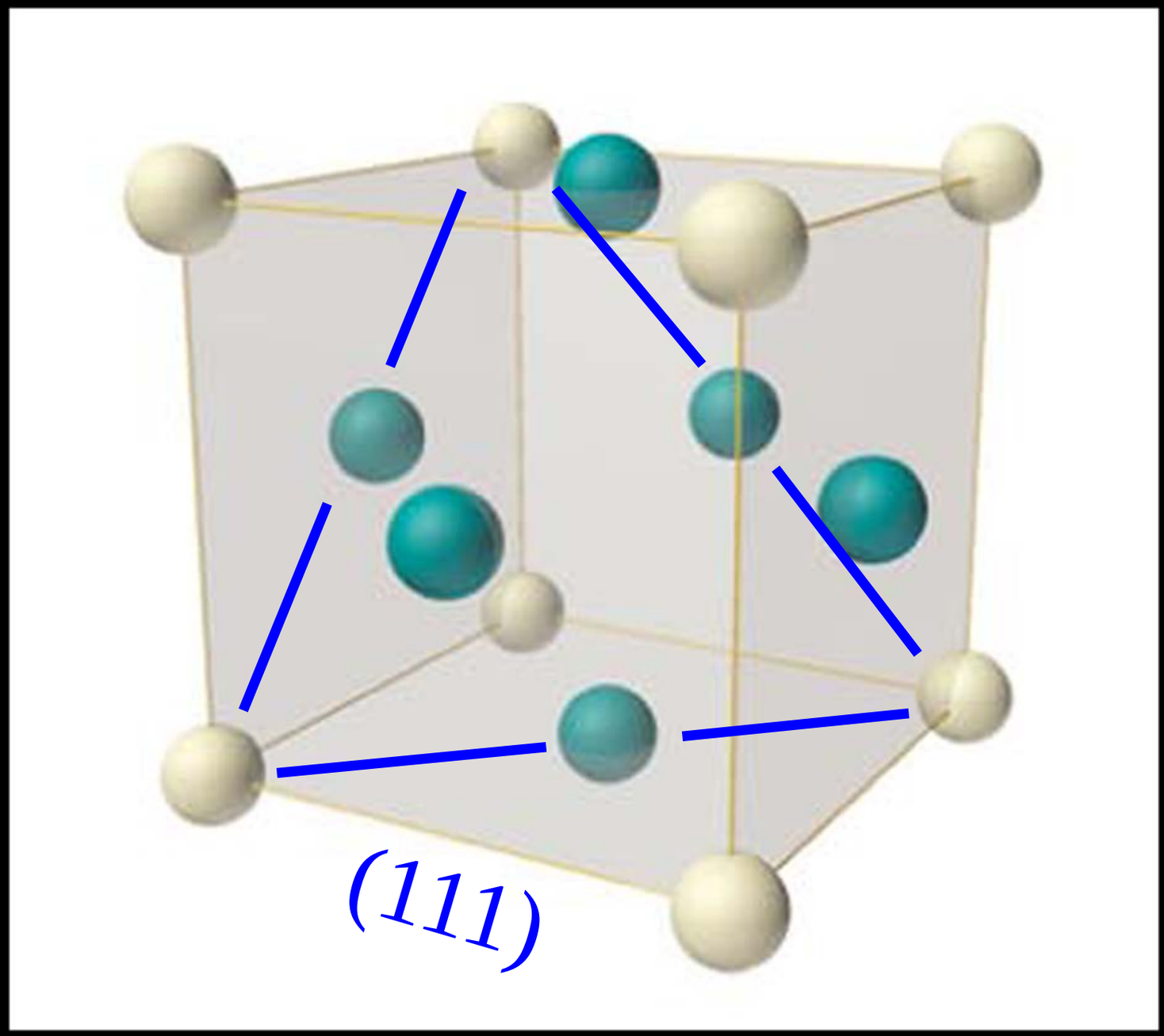
210	5	✓	✖	✖
211	6	✓	✓	✖
220	8	✓	✓	✓
300	9	✓	✖	✖
310	10	✓	✓	✖
311	11	✓	✖	✓
222	12	✓	✓	✓
320	13	✓	✖	✖
321	14	✓	✓	✖
400	16	✓	✓	✓





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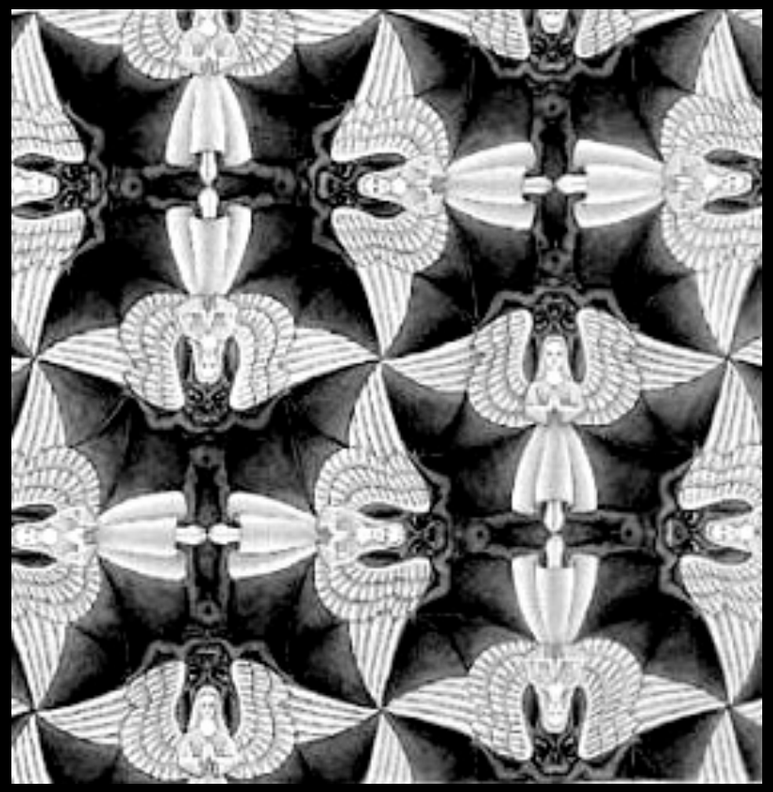
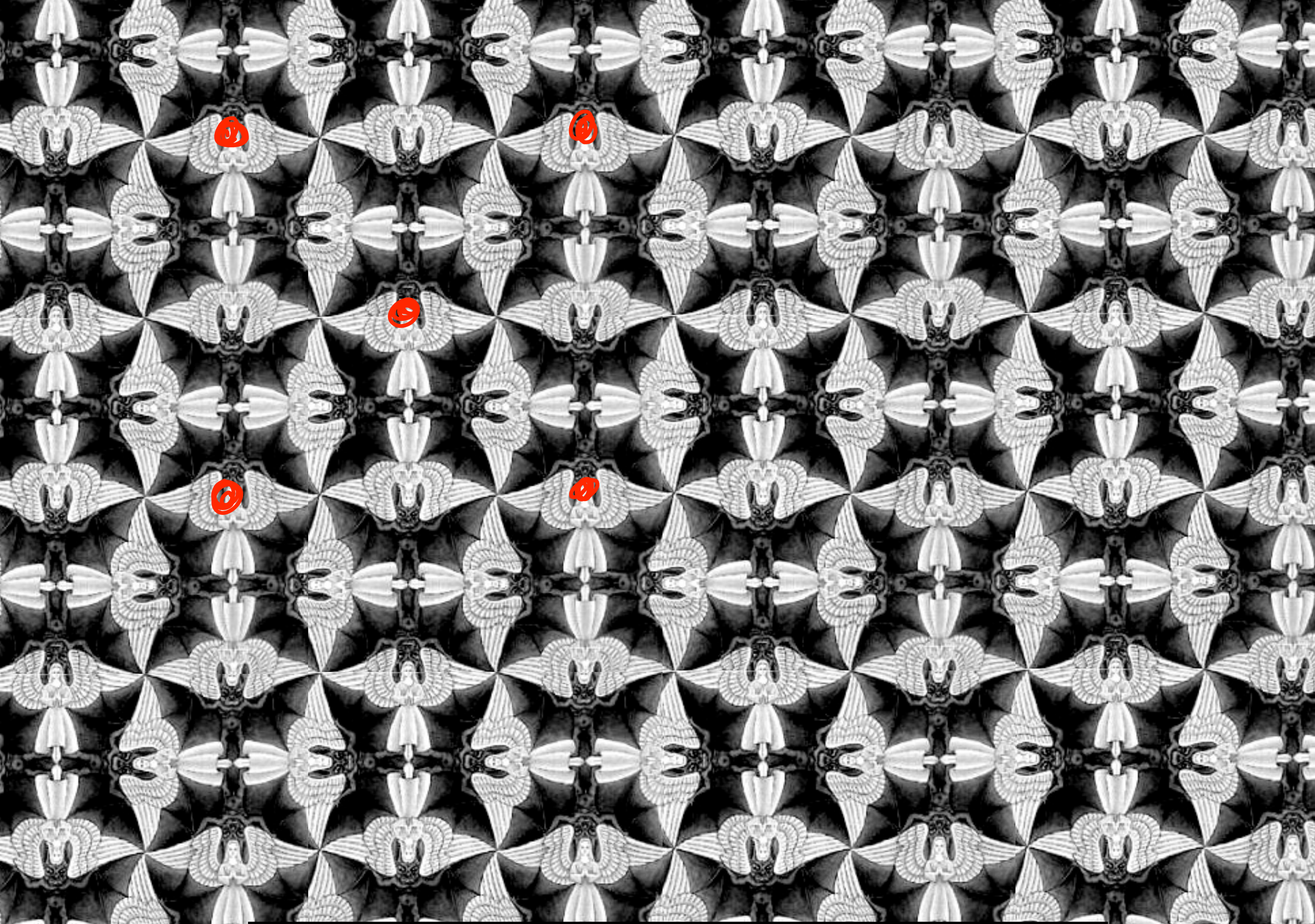
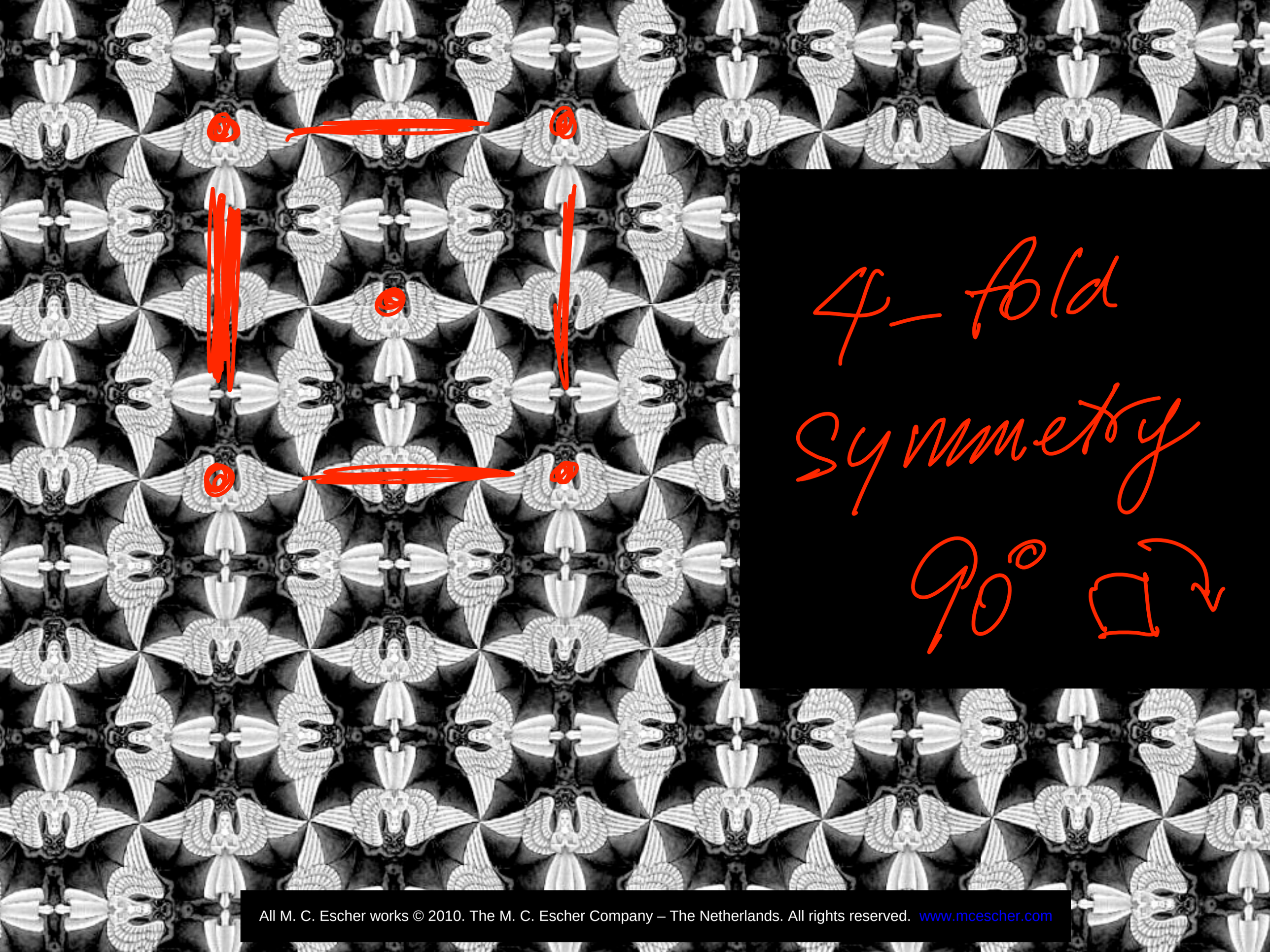
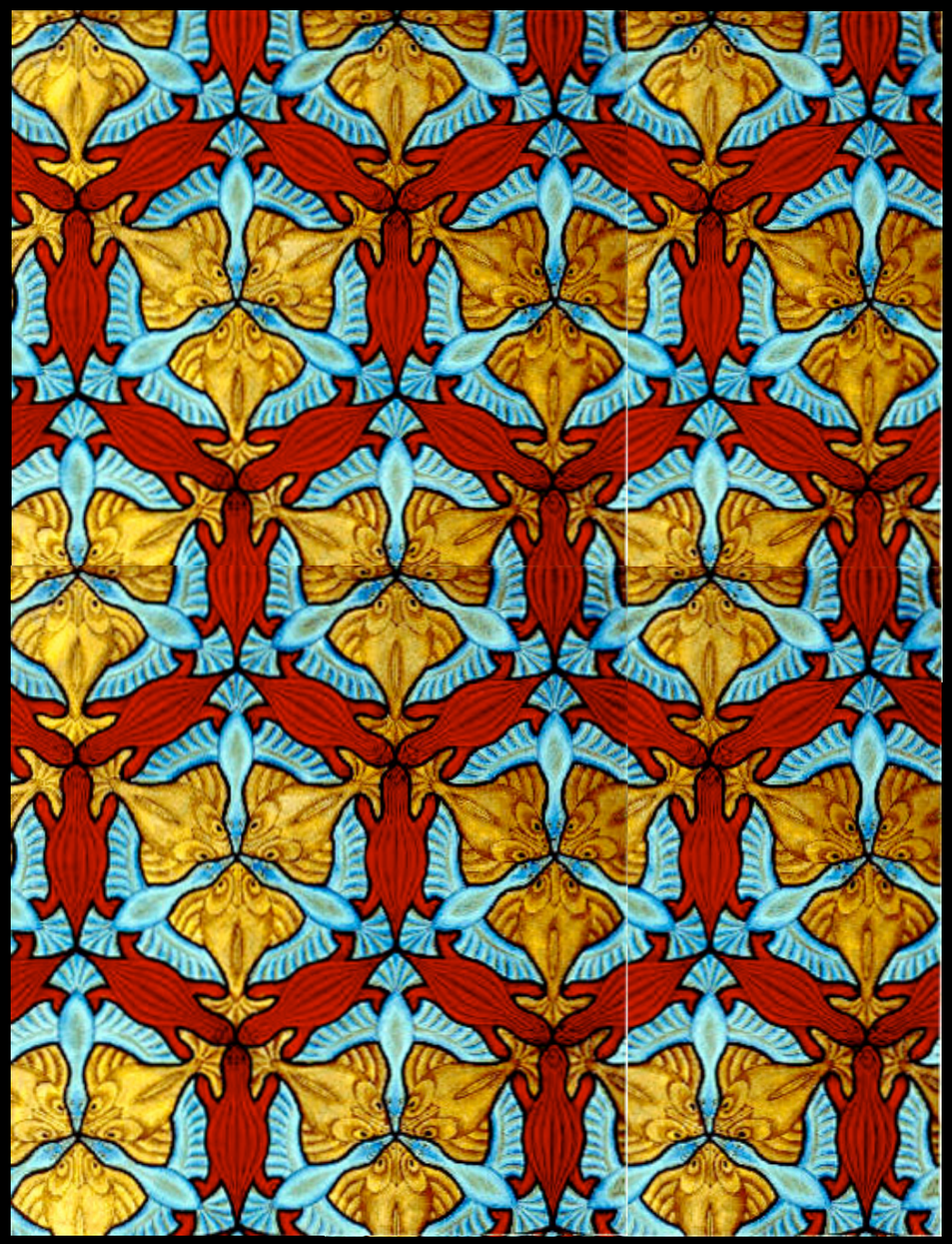
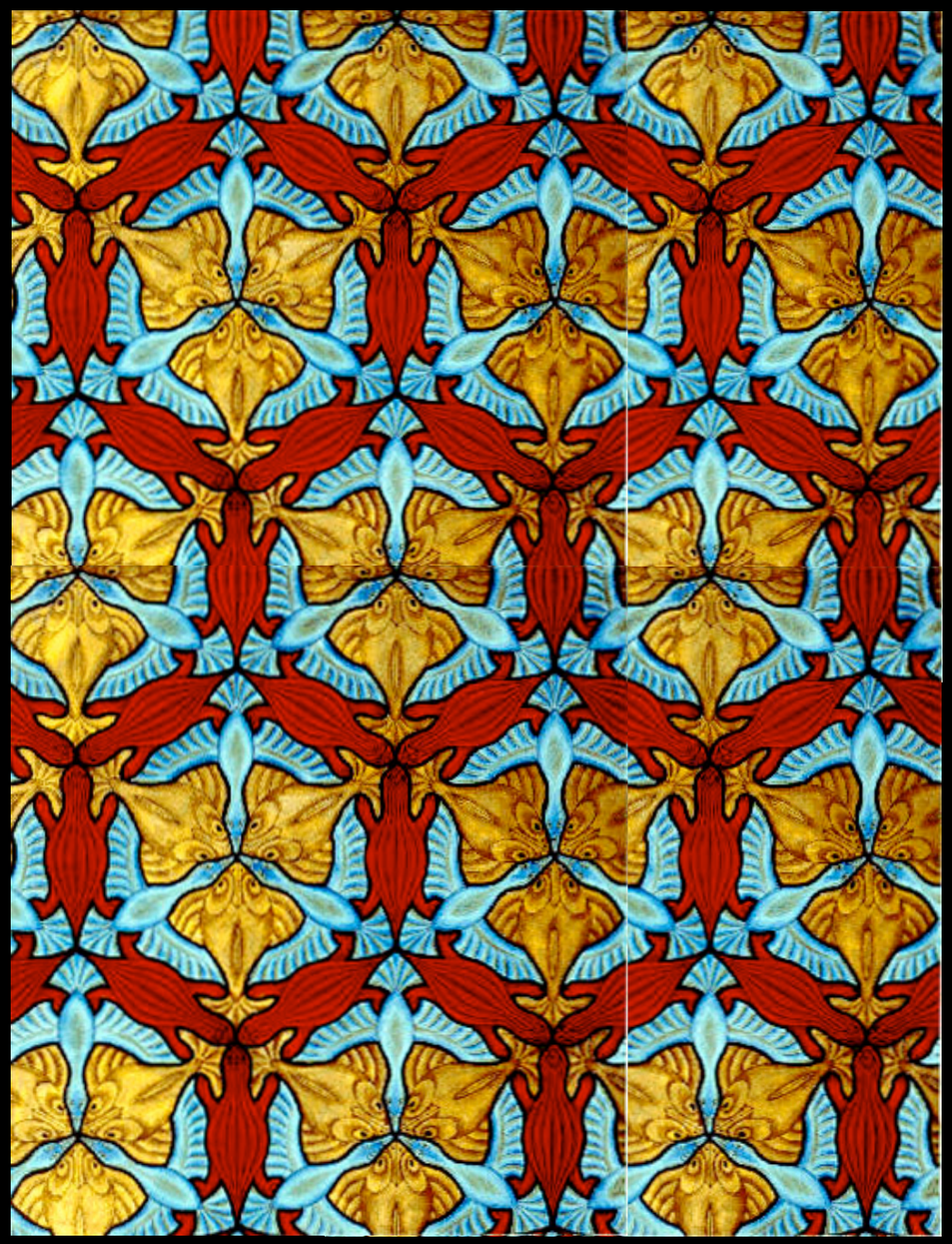




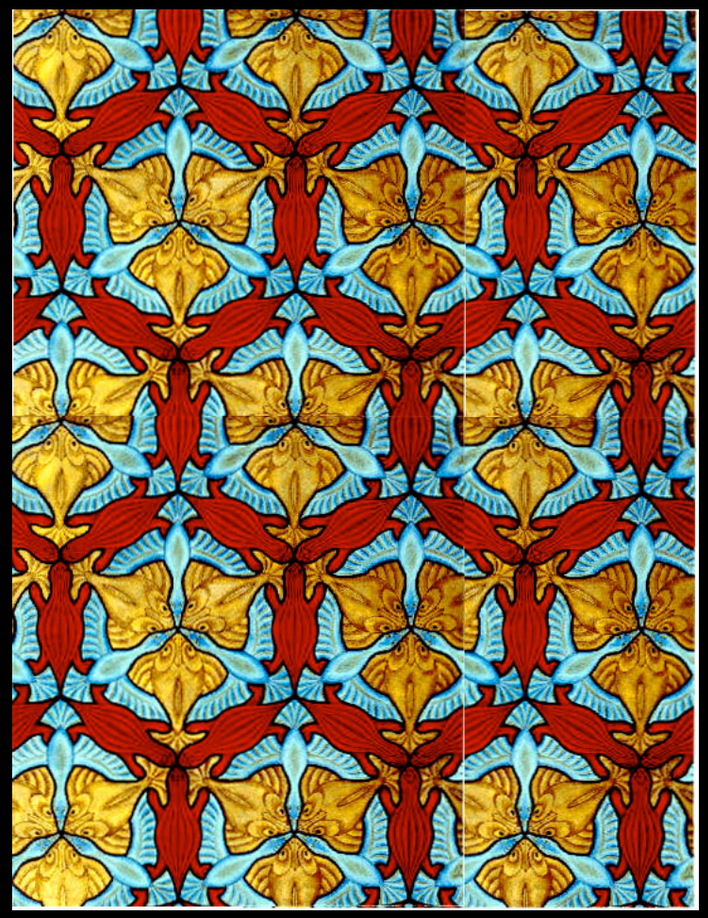


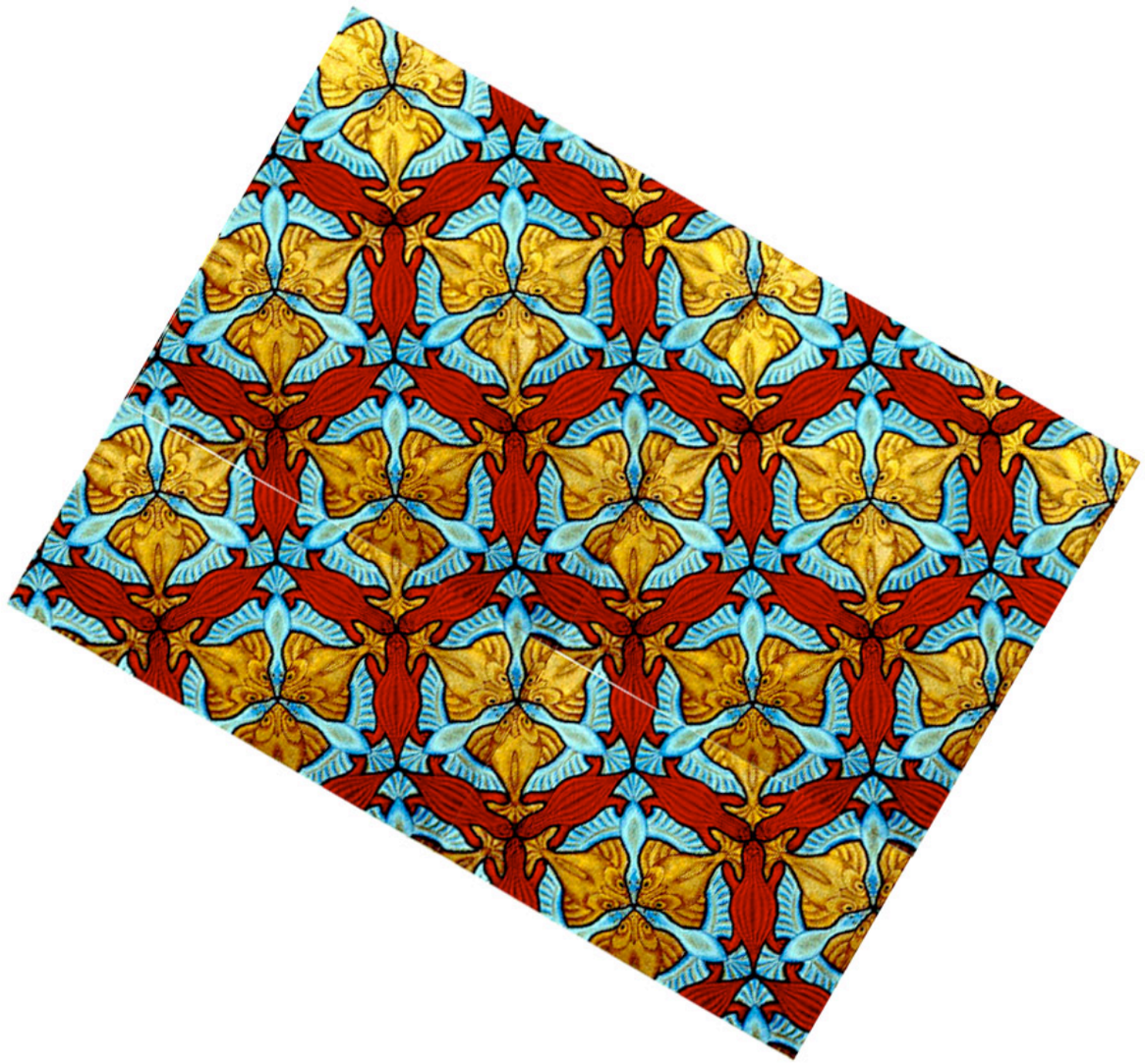




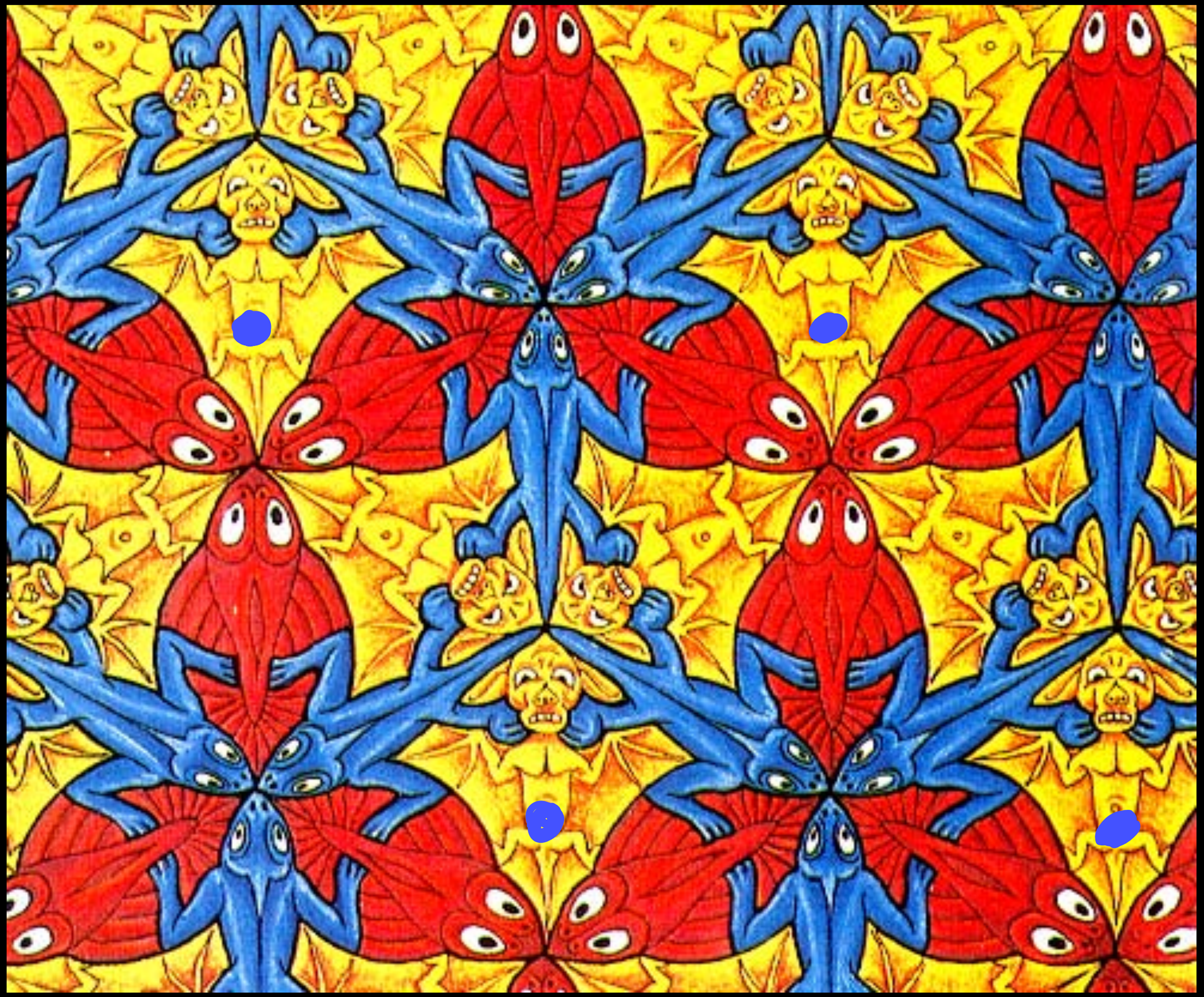
3-fold symmetry

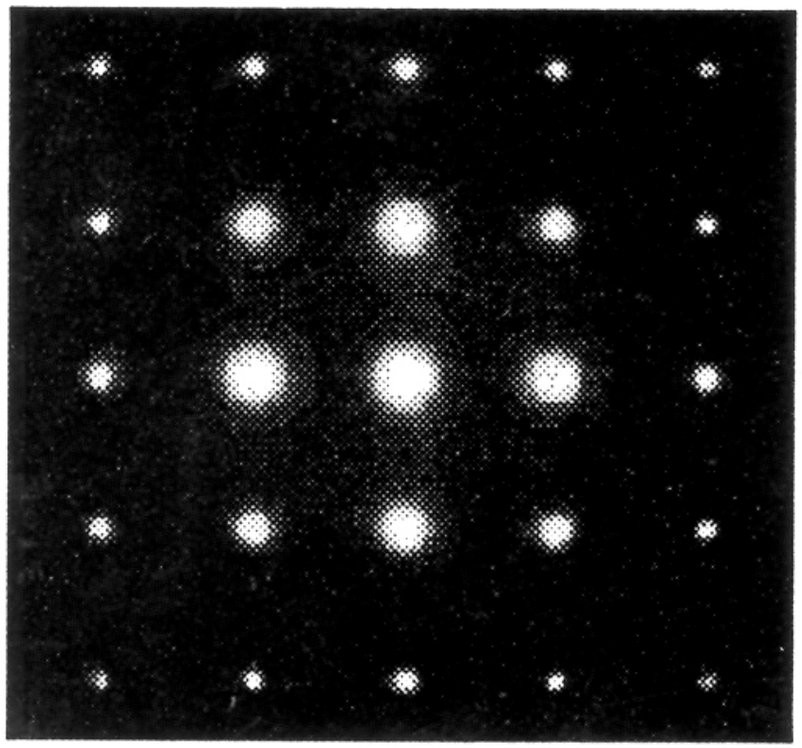
120°

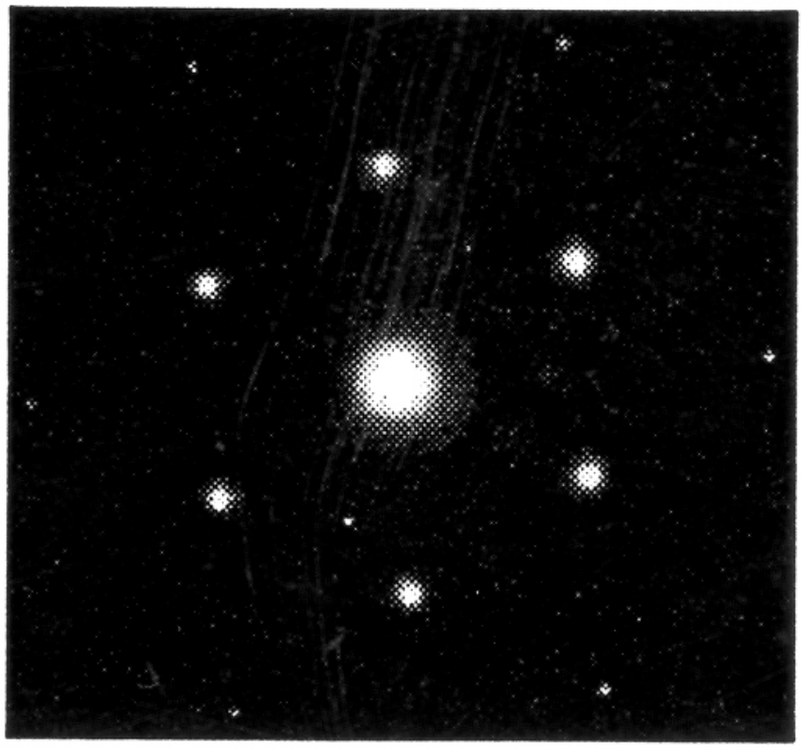


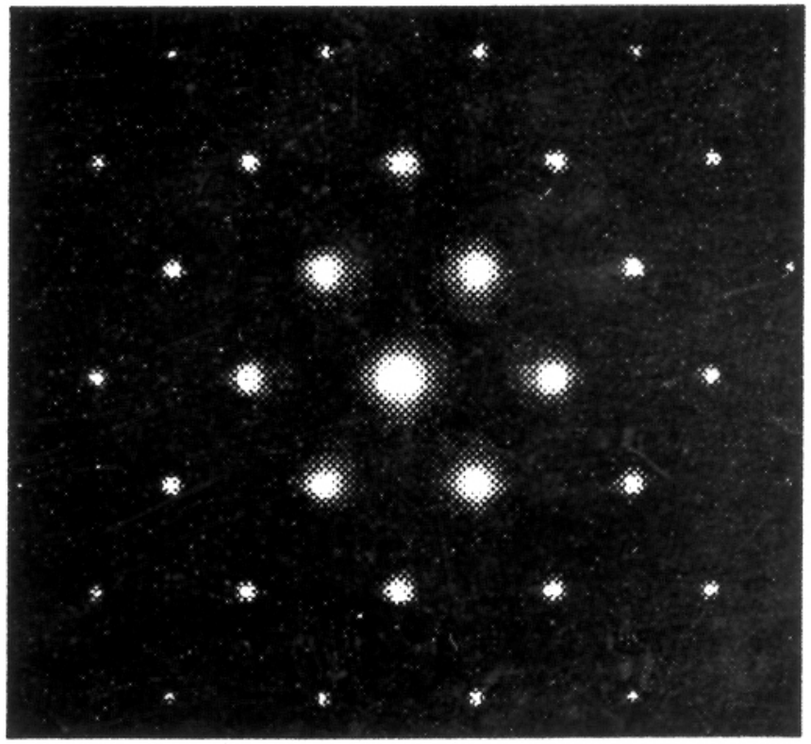


120° rotation

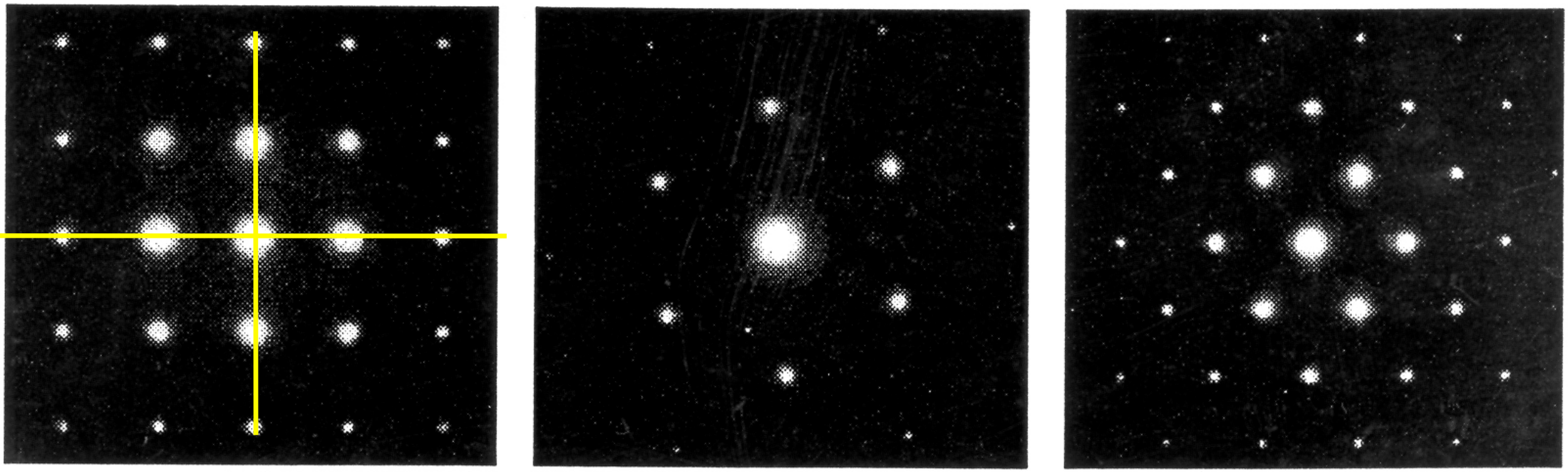








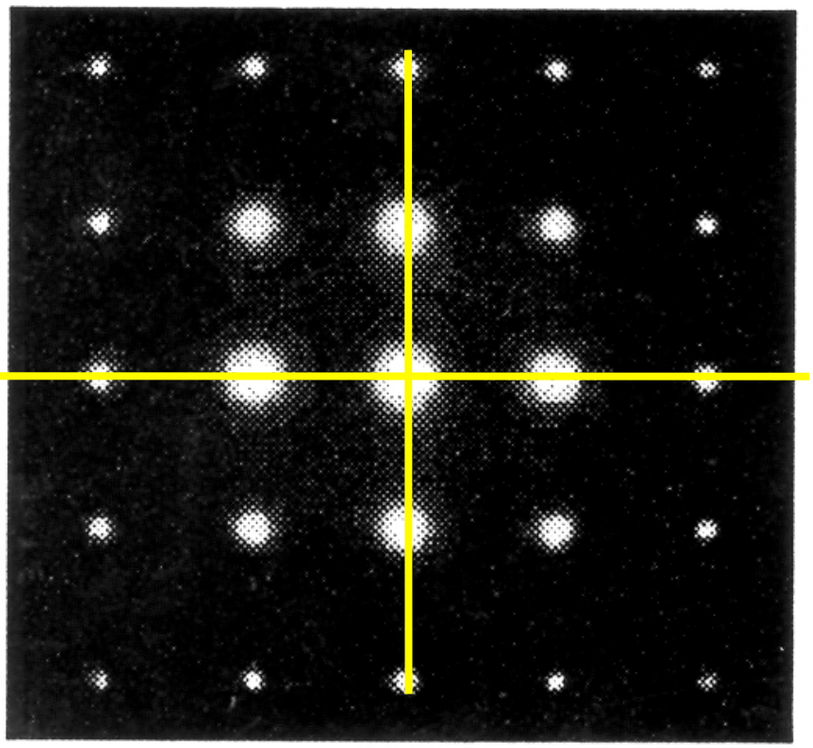
4-fold

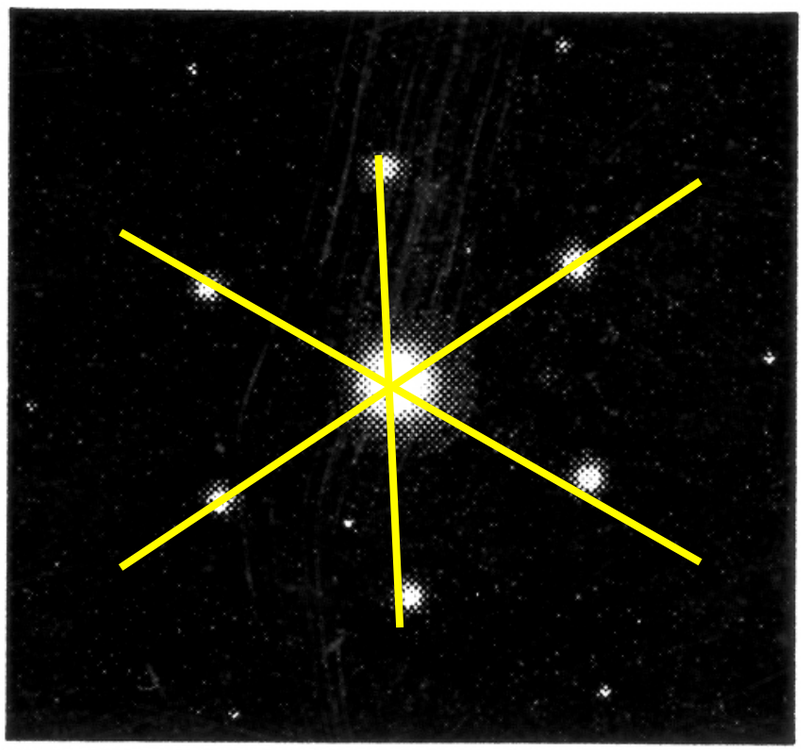


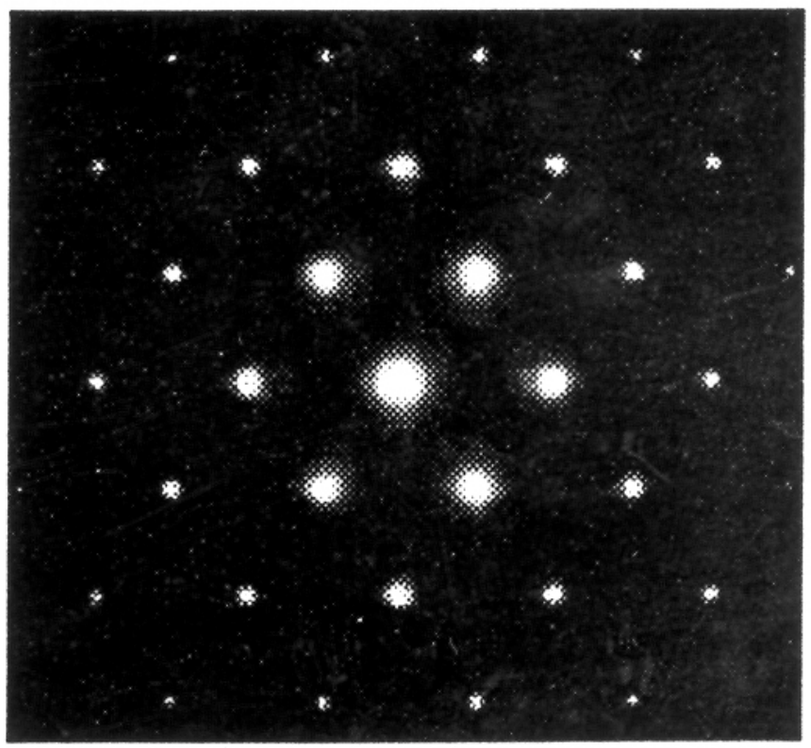
90º

4-fold

3-fold







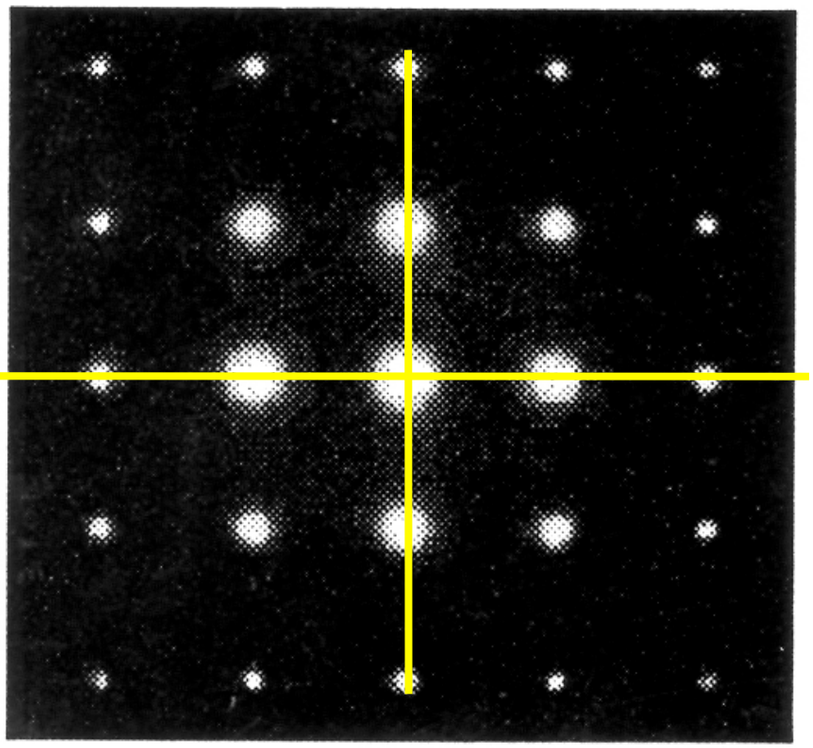
90º

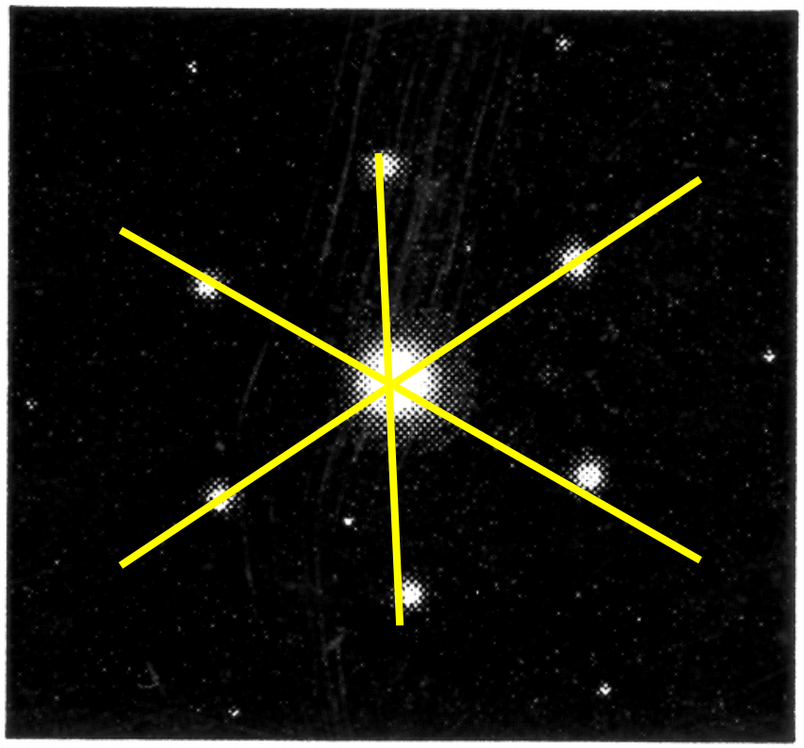
120º

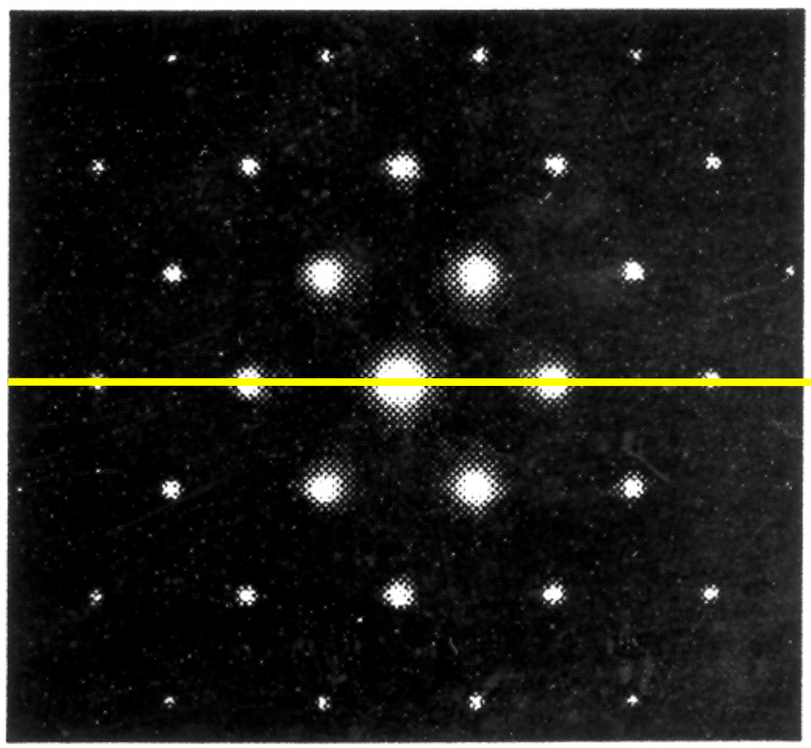
4-fold

3-fold

2-fold





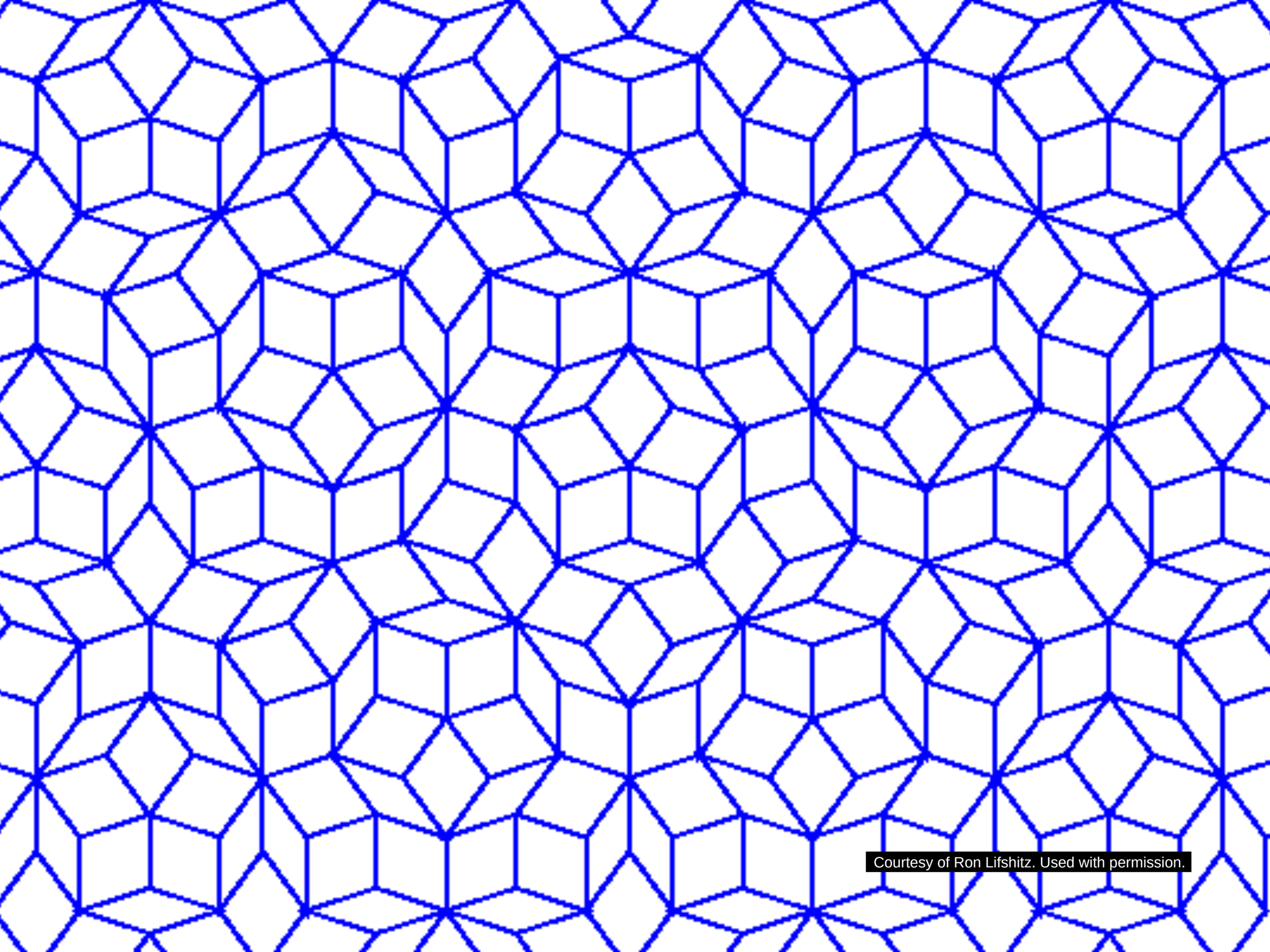


90º

120º

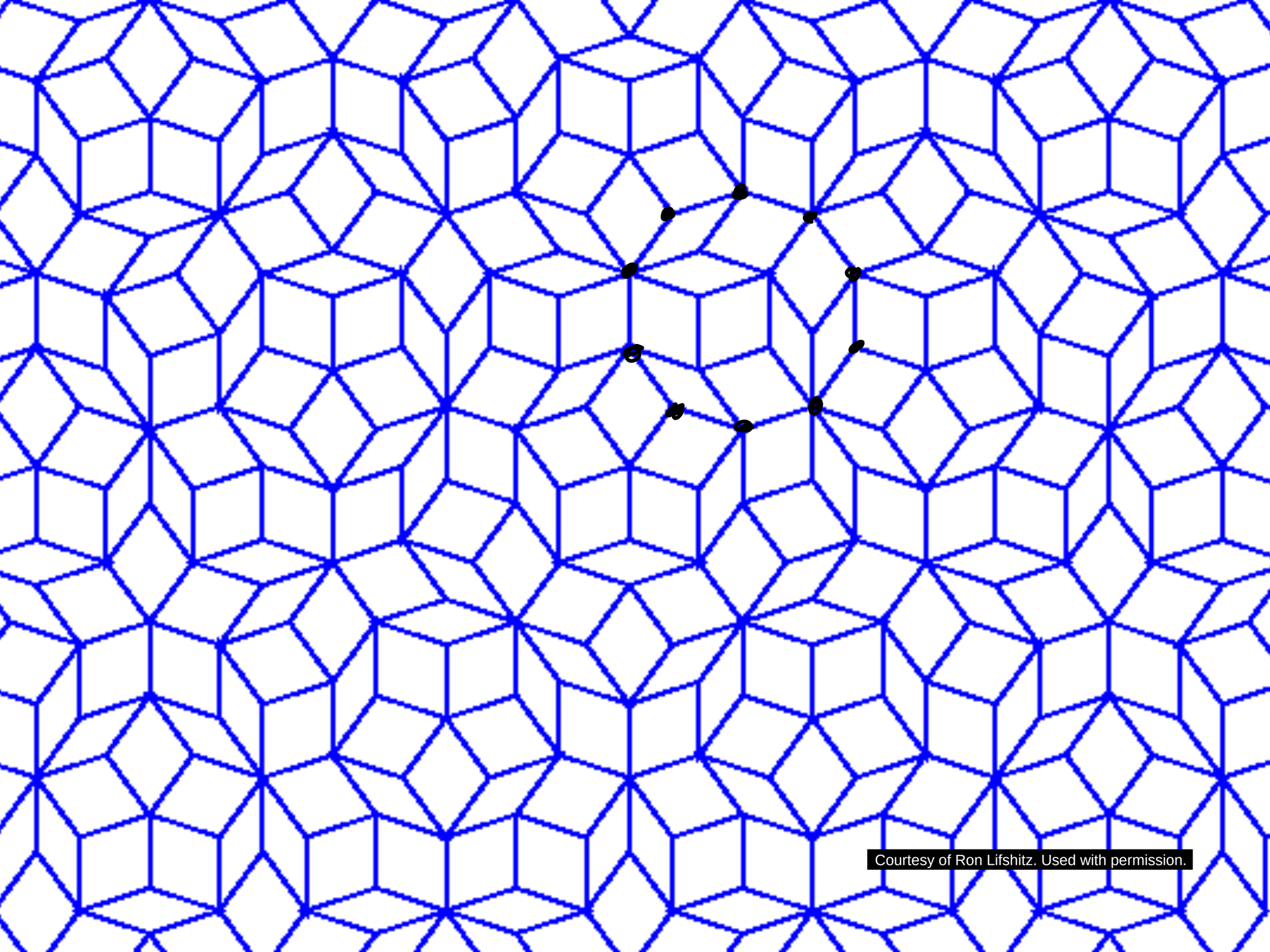
180º

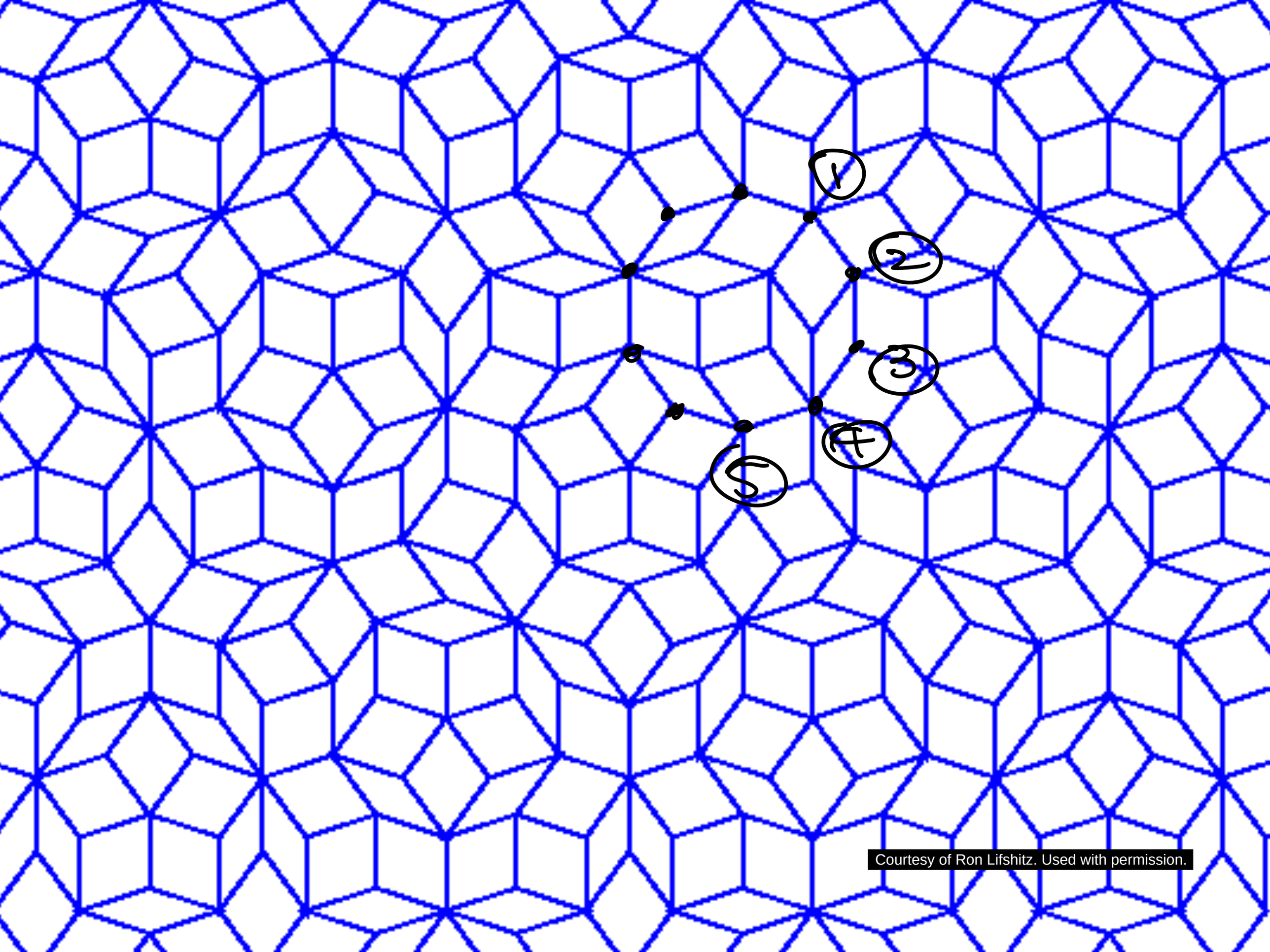
translational symmetry without rotational symmetry

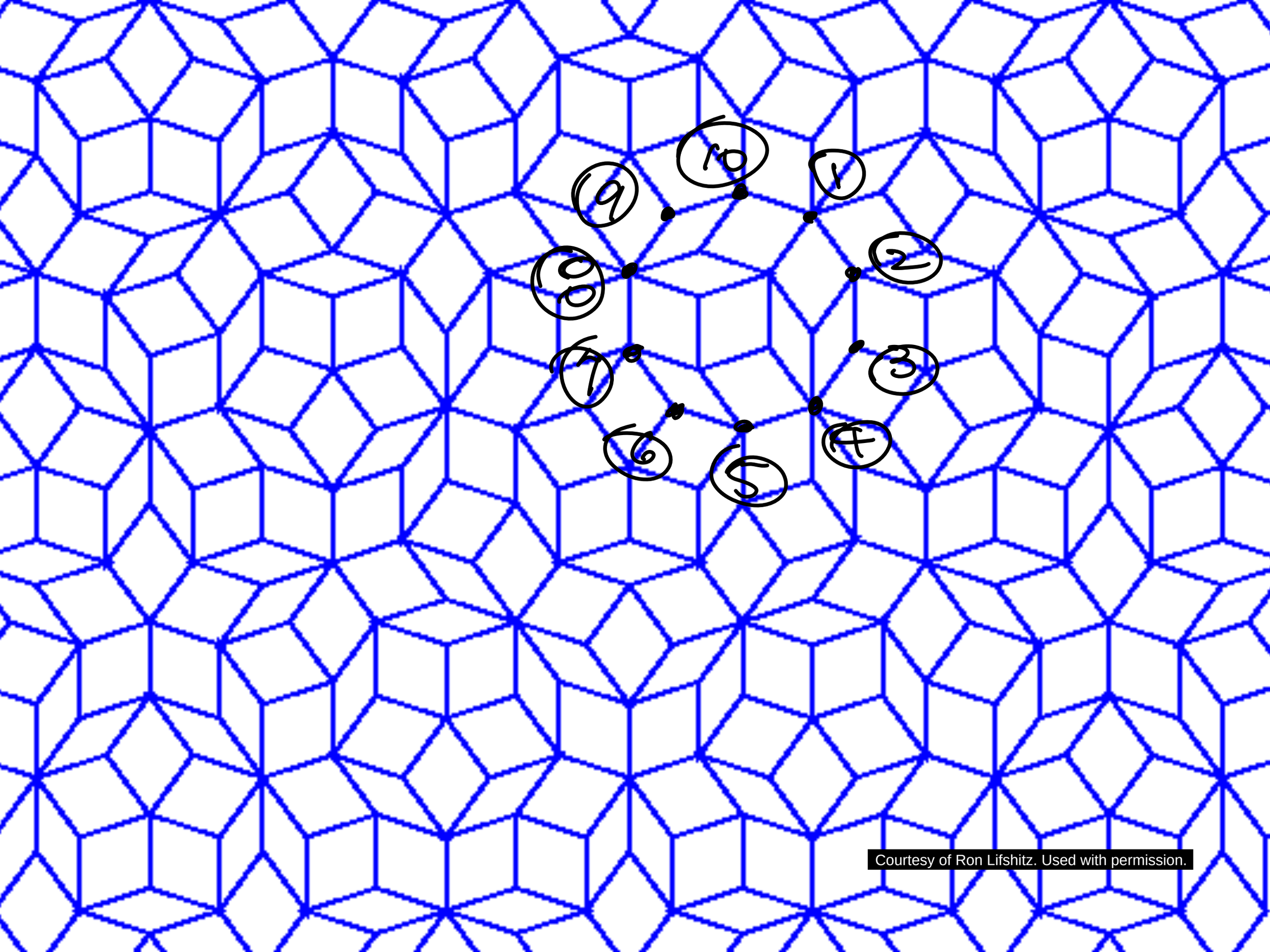


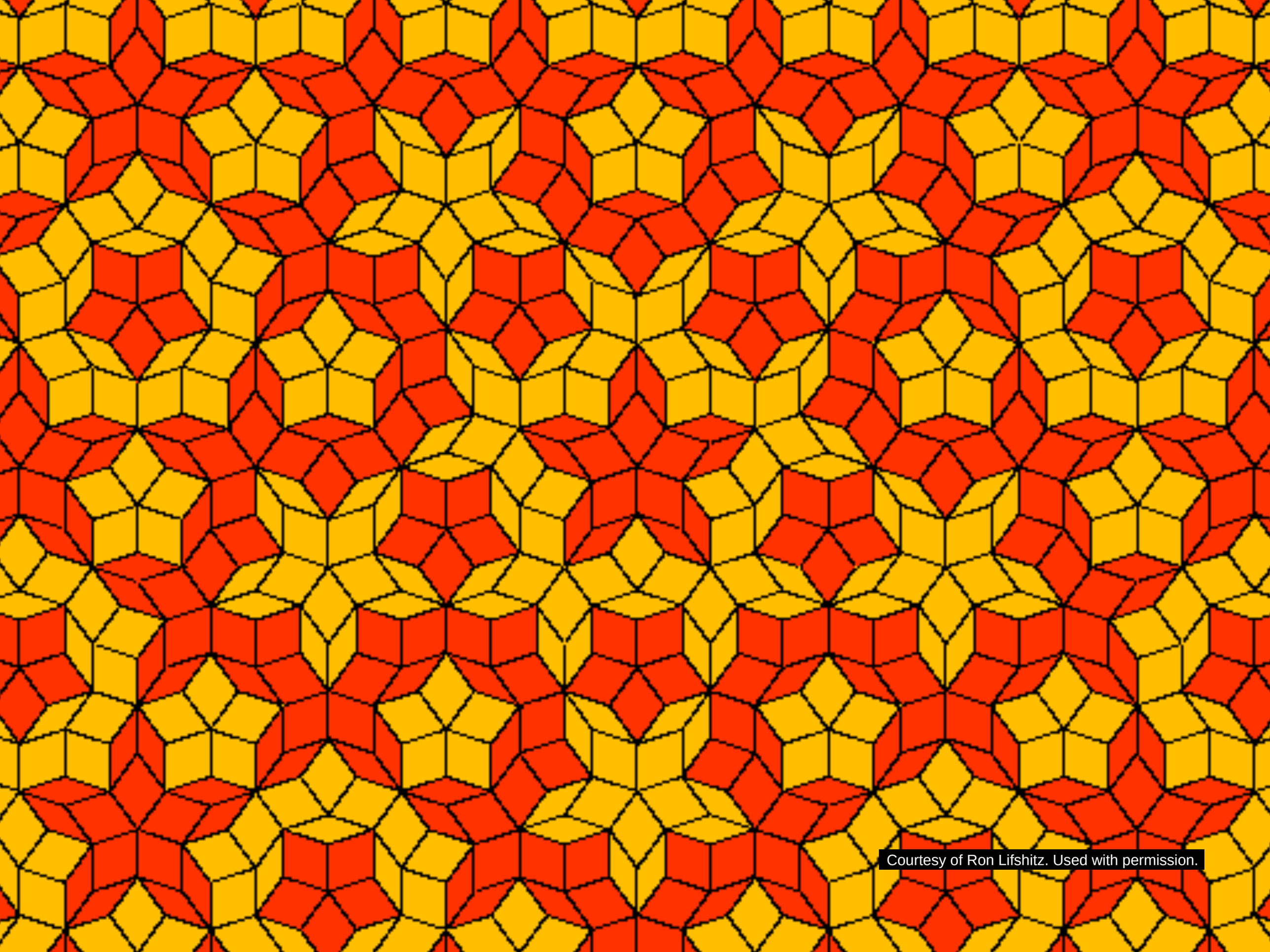
Penrose Tile

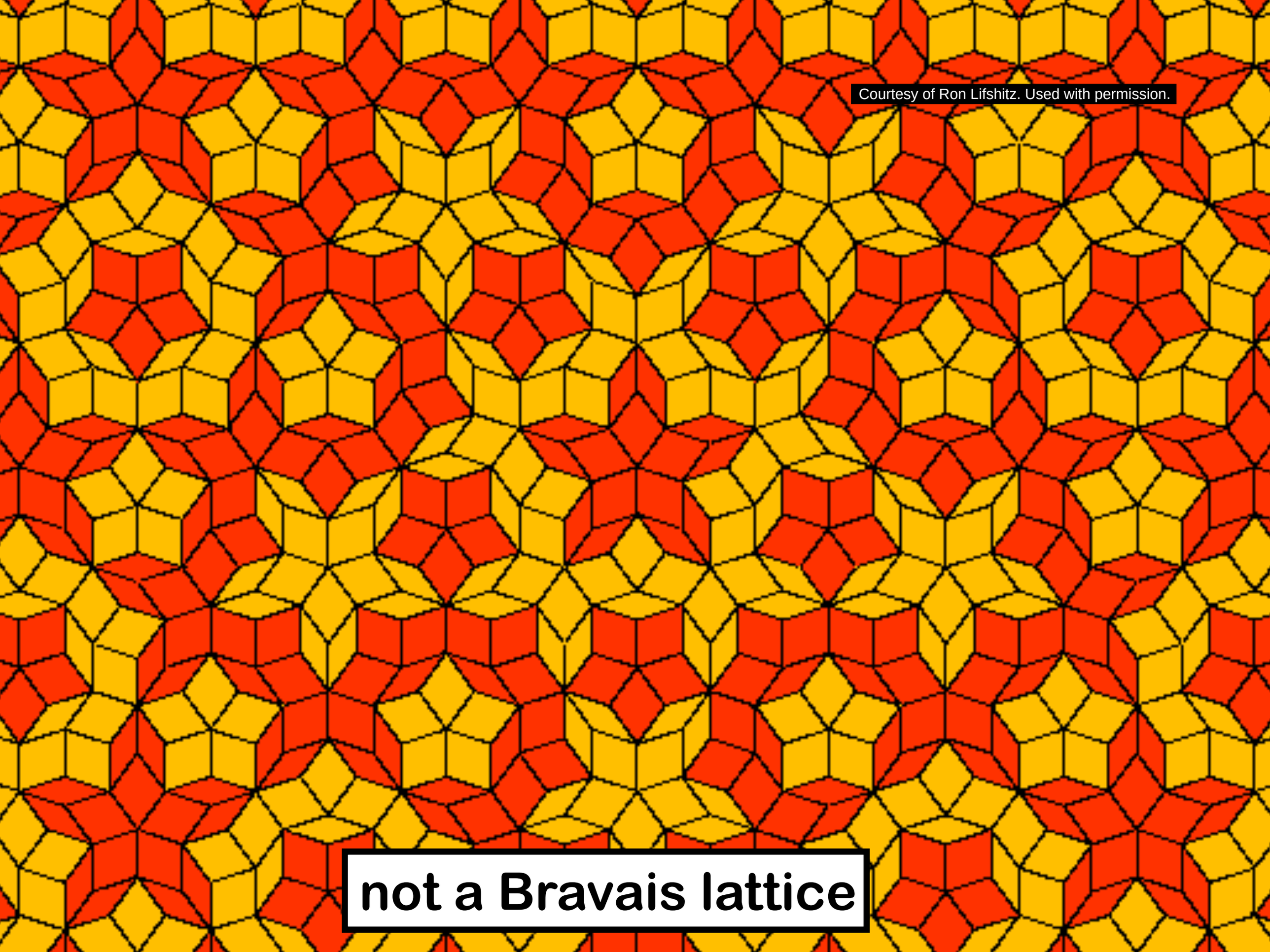
rotational symmetry without translational symmetry










Courtesy of Ron Lifshitz. Used with permission.
not a Bravais lattice

Taxonomy of Solids

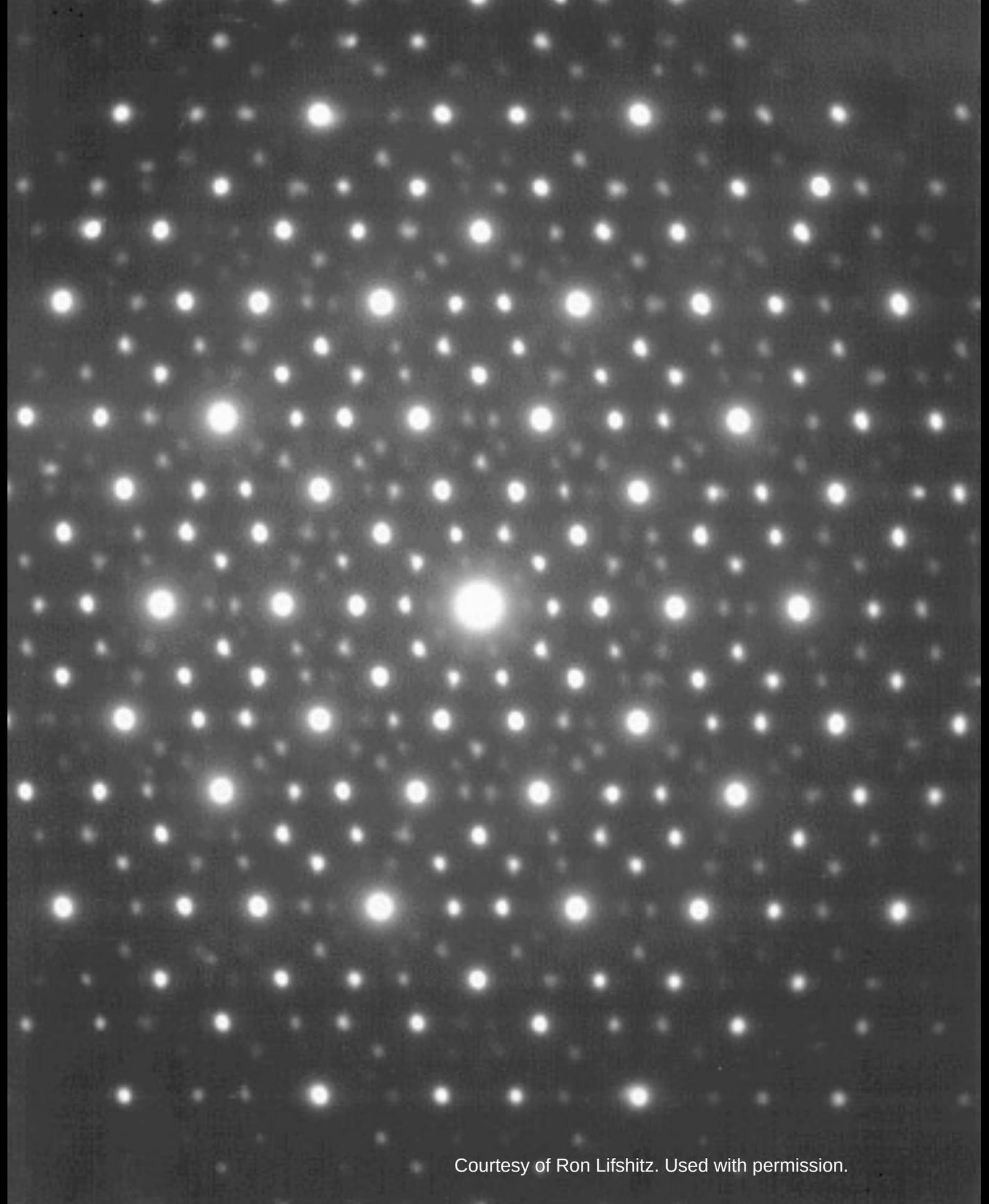
ordered	disordered
- unit cell	- no building block
- periodic	- no long-range order
- "crystal"	- "glass"

1982 Dan Schechtman (Technion) working at National Institute of Standards and Technology (NIST), Gaithersburg, MD

Al - Mn alloy:

- highly ordered
- symmetries impossible in a true crystal
  (5-fold rotational symmetry)
- lacks translational symmetry: ***aperiodic***

"quasicrystals"



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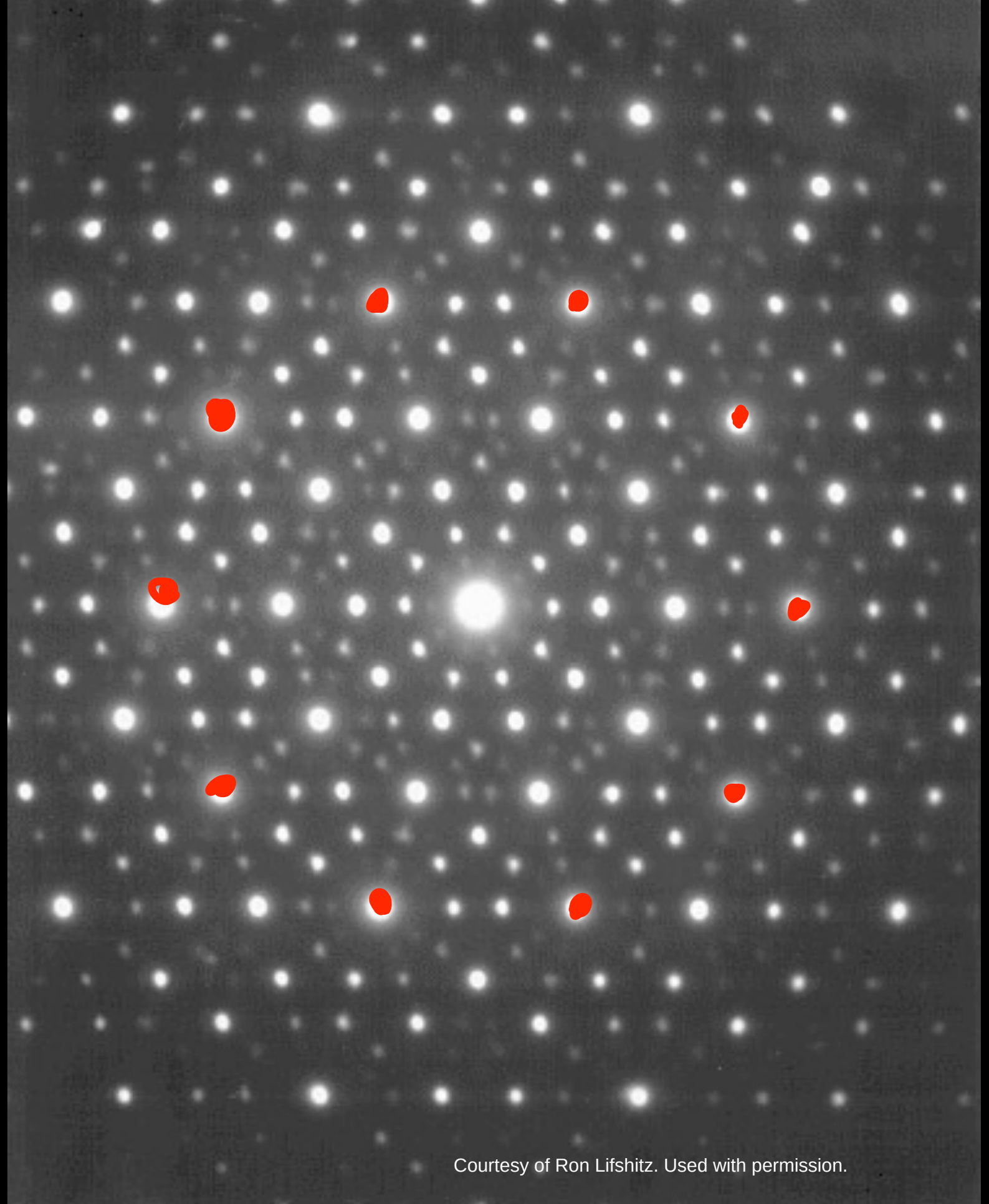

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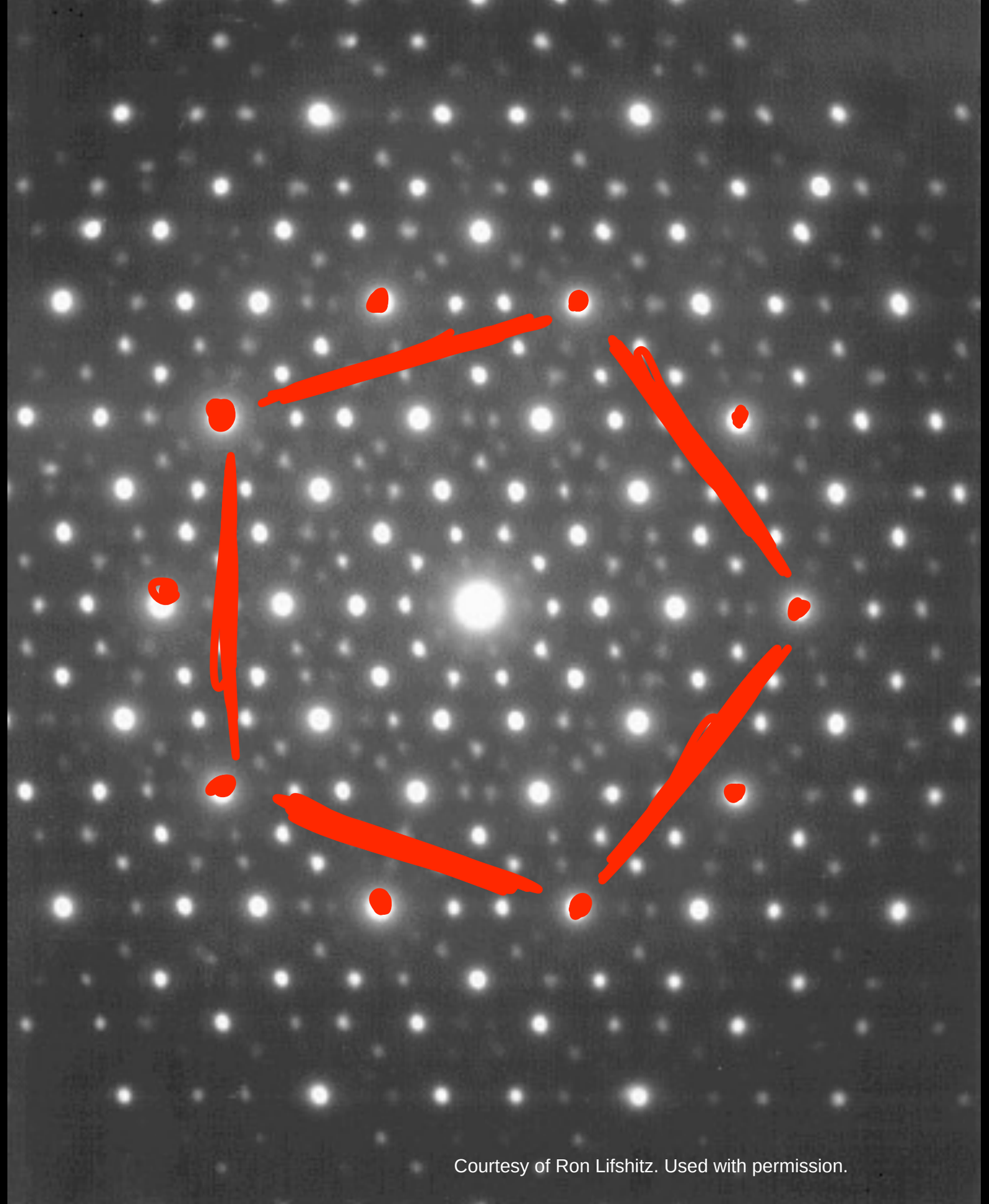
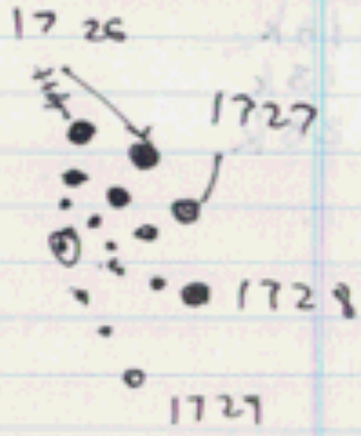


5-fold

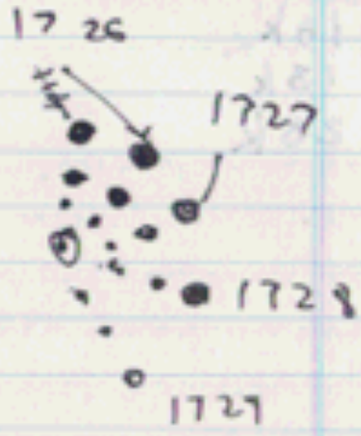
72º

Courtesy of Ron Lifshitz. Used with permission.



AL- 25 w/o Mn April 8, 82

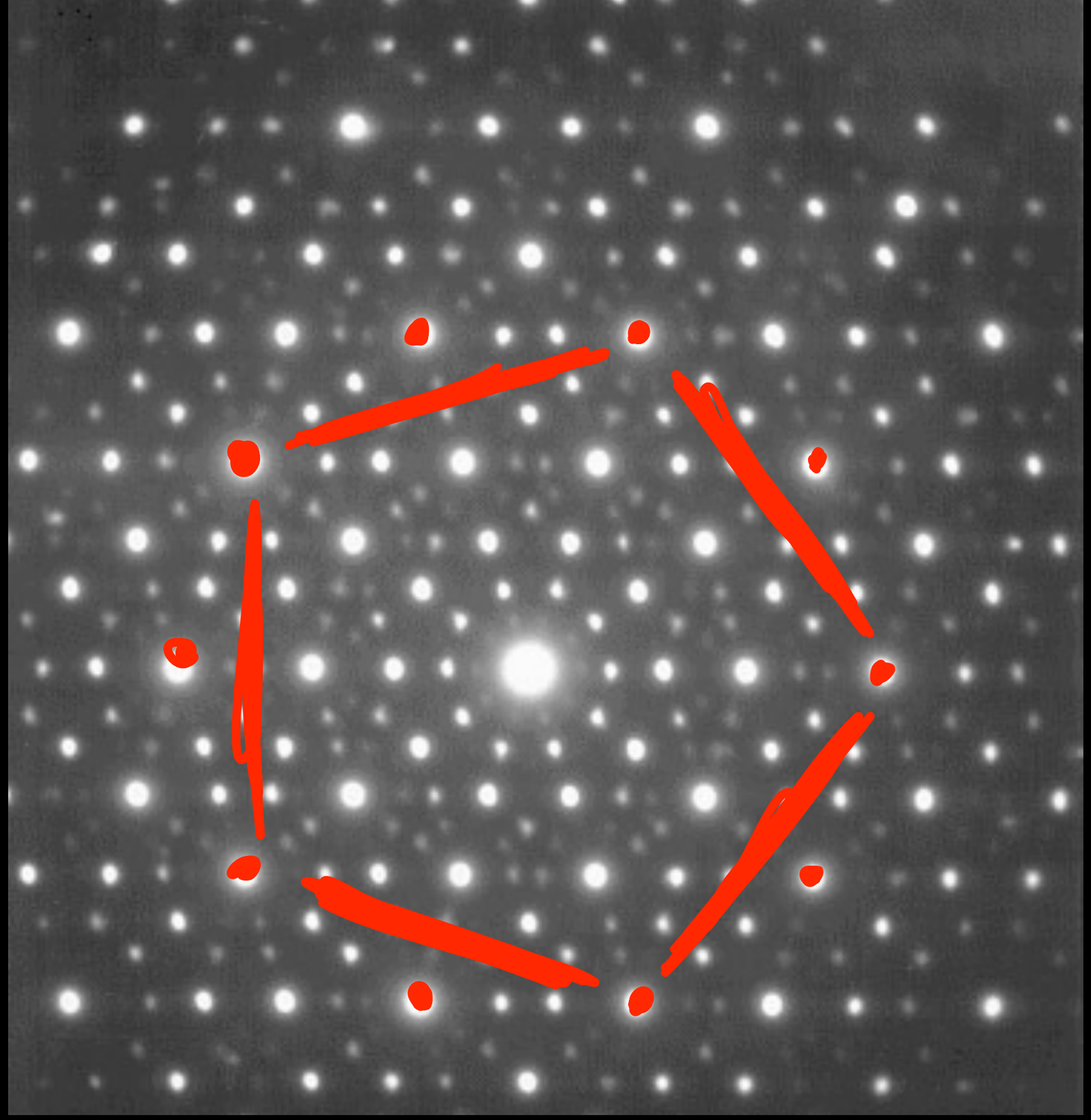
1720	SAD
1721	SAD
1722	28k
1723	17k
1724	36k
1725	SAD (10 Fold ???)
1726	36k DF
1727	36k DF
1728	36k DF
1729	36k DF
1730	SAD 2300
1731	" 1600
1732	36k BF
1733	100k BF
1734	100k BF
1735	100k BF
1736	SAD another ptcle.
1737	μdiff 800
1738	μdiff 1600
1739	" "
1740	SAD another area
1741	13k
1742	17k



AL- 25 w/o Mn

April 8, 82

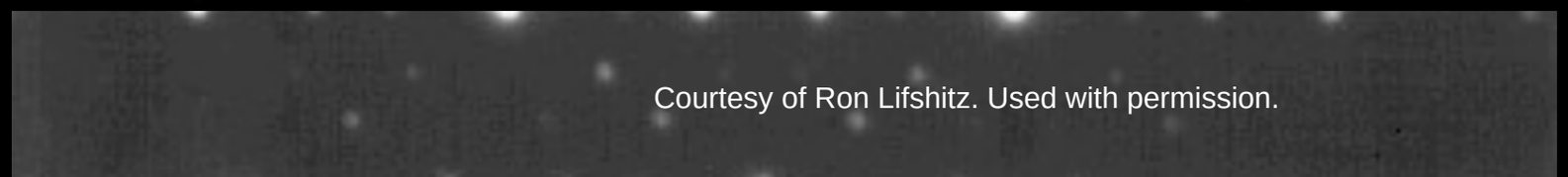
1720	SAD
1721	SAD
1722	28k
1723	17k
1724	36k
1725	SAD (10 Fold ???)
1726	36k DF
1727	36k DF
1728	36k DF
1729	36k DF
1730	SAD 2300
1731	" 1600
1732	36k BF
1733	100k BF
1734	100k BF
1735	100k BF
1736	SAD another ptcle.
1737	μdiff 800
1738	μdiff 1600
1739	" "
1740	SAD another area
1741	13k
1742	17k



5-fold

72º

“Mission Impossible” – an example of 5:4 time



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3.091SC Introduction to Solid State Chemistry

Fall 2009