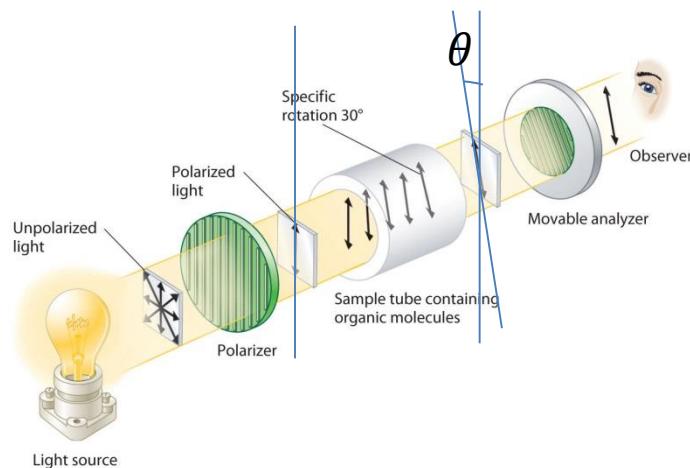


# Optical Activity, Mirror symmetry

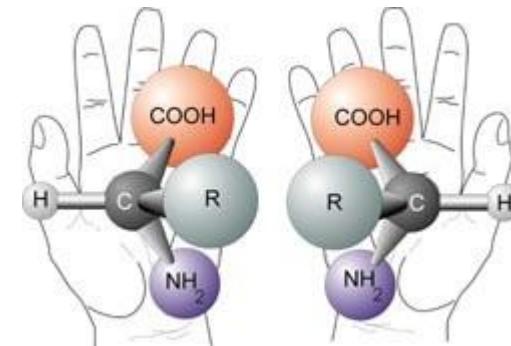
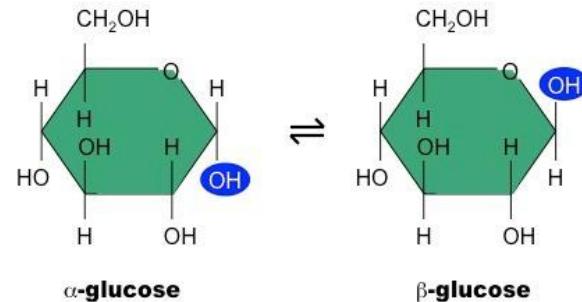
Seoncheol Cha  
24.Aug.2013.

# What is a Optical Activity? - Remind

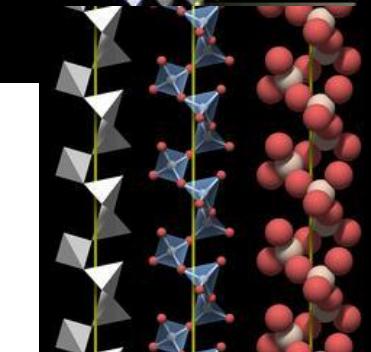
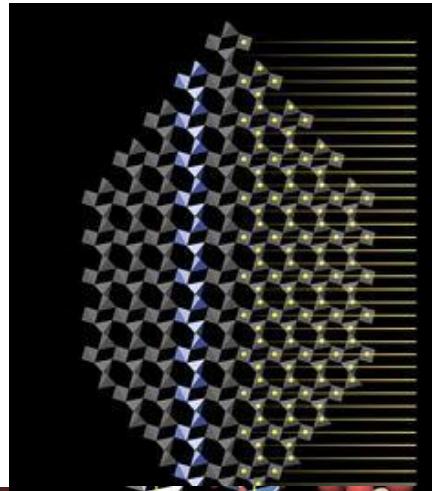
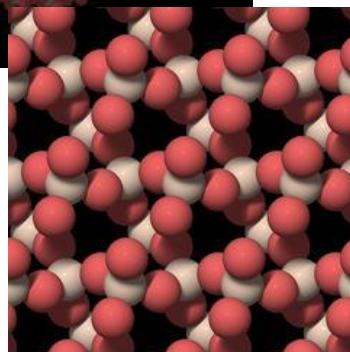
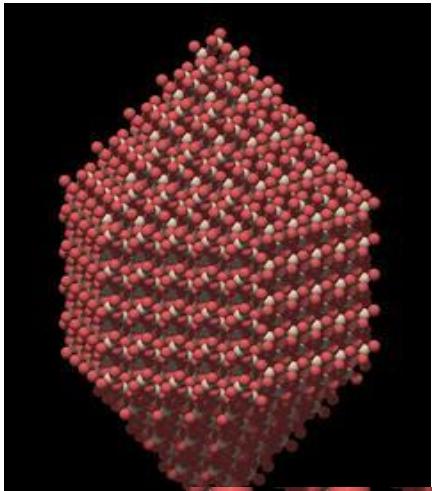
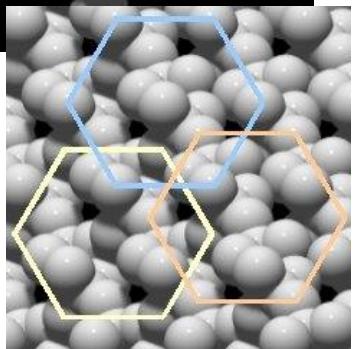
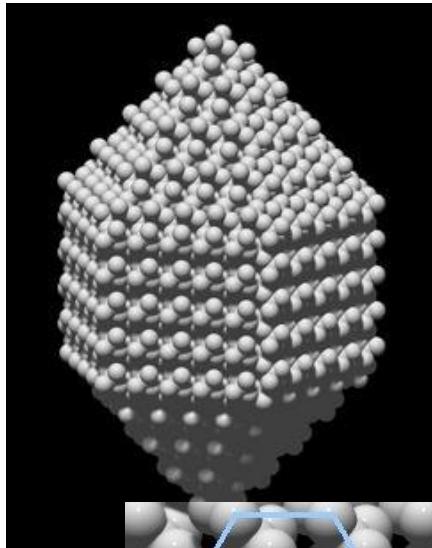
$$\theta = (n_R - n_L) \frac{\pi l}{\lambda}$$



Mirror image  
(Chiral center)



# Optical Activity of Quartz Crystal



# Optical Activity

$$\theta = (n_R - n_L) \frac{\pi l}{\lambda}$$

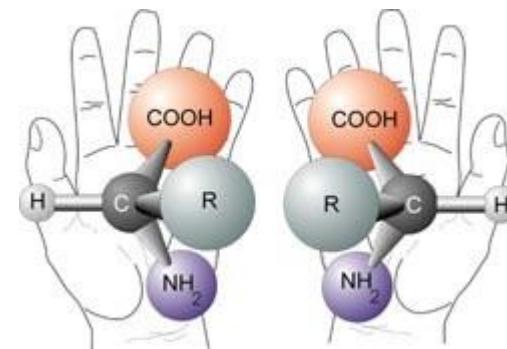
Where does different  $n_R$  and  $n_L$  come from?

$$\vec{\chi} = \begin{pmatrix} \chi_{11} & i\chi_{12} & 0 \\ -i\chi_{12} & \chi_{11} & 0 \\ 0 & 0 & \chi_{33} \end{pmatrix}$$

$$n_R = \sqrt{1 + \chi_{11} + \chi_{12}}$$

$$n_L = \sqrt{1 + \chi_{11} - \chi_{12}}$$

Only materials having chiral center have non-zero  $\chi_{12}$



# Optical Activity

$$\vec{\chi} = \begin{pmatrix} \chi_{11} & i\chi_{12} & 0 \\ -i\chi_{12} & \chi_{11} & 0 \\ 0 & 0 & \chi_{33} \end{pmatrix}$$

$$n_R = \sqrt{1 + \chi_{11} + \chi_{12}}$$

$$n_L = \sqrt{1 + \chi_{11} - \chi_{12}}$$

$$\vec{k} \times (\vec{k} \times \vec{E}) + \frac{\omega^2}{c^2} \vec{E} = -\frac{\omega^2}{c^2} \vec{\chi} \vec{E}$$

$$-k^2 E_x + \frac{\omega^2}{c^2} E_x = -\frac{\omega^2}{c^2} (\chi_{11} E_x + i\chi_{12} E_y)$$

$$-k^2 E_y + \frac{\omega^2}{c^2} E_y = -\frac{\omega^2}{c^2} (-i\chi_{12} E_x + \chi_{11} E_y)$$

$$\frac{\omega^2}{c^2} E_z = -\frac{\omega^2}{c^2} \chi_{33} E_x$$

$$\begin{vmatrix} -k^2 + \frac{\omega^2}{c^2} (1 + \chi_{11}) & i \frac{\omega^2}{c^2} \chi_{12} \\ -i \frac{\omega^2}{c^2} \chi_{12} & -k^2 + \frac{\omega^2}{c^2} (1 + \chi_{11}) \end{vmatrix} = 0$$

# Optical Activity

$$k = \frac{\omega}{c} \sqrt{1 + \chi_{11} \pm \chi_{12}}$$

$$E_x = \pm i E_y$$

$$\vec{\chi} = \begin{pmatrix} \chi_{11} & i\chi_{12} & 0 \\ -i\chi_{12} & \chi_{11} & 0 \\ 0 & 0 & \chi_{33} \end{pmatrix}$$

$$n_R = \sqrt{1 + \chi_{11} + \chi_{12}}$$

$$n_L = \sqrt{1 + \chi_{11} - \chi_{12}}$$

$$\begin{aligned} \vec{k} \times (\vec{k} \times \vec{E}) + \frac{\omega^2}{c^2} \vec{E} &= -\frac{\omega^2}{c^2} \vec{\chi} \vec{E} \\ -k^2 E_x + \frac{\omega^2}{c^2} E_x &= -\frac{\omega^2}{c^2} (\chi_{11} E_x + i\chi_{12} E_y) \\ -k^2 E_y + \frac{\omega^2}{c^2} E_y &= -\frac{\omega^2}{c^2} (-i\chi_{12} E_x + \chi_{11} E_y) \end{aligned}$$

$$\frac{\omega^2}{c^2} E_z = -\frac{\omega^2}{c^2} \chi_{33} E_x$$

$$\begin{vmatrix} -k^2 + \frac{\omega^2}{c^2} (1 + \chi_{11}) & i \frac{\omega^2}{c^2} \chi_{12} \\ -i \frac{\omega^2}{c^2} \chi_{12} & -k^2 + \frac{\omega^2}{c^2} (1 + \chi_{11}) \end{vmatrix} = 0$$

# **Optical Activity**

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# Birefringence

$$\vec{\chi} = \begin{pmatrix} \chi_{11} & 0 & 0 \\ 0 & \chi_{22} & 0 \\ 0 & 0 & \chi_{33} \end{pmatrix}$$

$$k = \frac{\omega}{c} \sqrt{1 + \chi_{11}}$$

$$k = \frac{\omega}{c} \sqrt{1 + \chi_{22}}$$

$$-k^2 E_x + \frac{\omega^2}{c^2} E_x = -\frac{\omega^2}{c^2} \chi_{11} E_x$$

$$-k^2 E_y + \frac{\omega^2}{c^2} E_y = -\frac{\omega^2}{c^2} \chi_{22} E_y$$

$$\frac{\omega^2}{c^2} E_z = -\frac{\omega^2}{c^2} \chi_{33} E_x$$

# Birefringence

Jones Matrix for birefringent material

$$\begin{pmatrix} e^{i\phi_x} & 0 \\ 0 & e^{i\phi_y} \end{pmatrix}$$

under all rotation

$$\begin{pmatrix} e^{i\phi_x}\cos^2\theta + e^{i\phi_y}\sin^2\theta & (e^{i\phi_x} - e^{i\phi_y})\cos\theta\sin\theta \\ (e^{i\phi_x} - e^{i\phi_y})\cos\theta\sin\theta & e^{i\phi_x}\sin^2\theta + e^{i\phi_y}\cos^2\theta \end{pmatrix}$$

for  $\phi_x - \phi_y = \pi/4$

$$\begin{pmatrix} \cos^2\theta - i\sin^2\theta & (-1+i)\cos\theta\sin\theta \\ (1+i)\cos\theta\sin\theta & \pm(-\sin^2\theta + i\cos^2\theta) \end{pmatrix} \quad \begin{pmatrix} 1 & \pm i \\ \pm i & 1 \end{pmatrix}$$

for  $\phi_x - \phi_y = \pi/2$

$$\begin{pmatrix} \cos 2\theta & \sin 2\theta \\ \sin 2\theta & -\cos 2\theta \end{pmatrix}$$

# Length dependence of Birefringence and Optical Activity

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$$\begin{pmatrix} e^{i\phi_x}\cos^2\theta + e^{i\phi_y}\sin^2\theta & (e^{i\phi_x} - e^{i\phi_y})\cos\theta\sin\theta \\ (e^{i\phi_x} - e^{i\phi_y})\cos\theta\sin\theta & e^{i\phi_x}\sin^2\theta + e^{i\phi_y}\cos^2\theta \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$
$$= \begin{pmatrix} e^{i\phi_x}\cos^2\theta + e^{i\phi_y}\sin^2\theta \\ (e^{i\phi_x} - e^{i\phi_y})\cos\theta\sin\theta \end{pmatrix}$$
$$= e^{i\phi_x} \begin{pmatrix} \cos^2\theta + e^{i(\phi_y-\phi_x)}\sin^2\theta \\ (1 - e^{i(\phi_y-\phi_x)})\cos\theta\sin\theta \end{pmatrix}$$

# Length dependence of Birefringence and Optical Activity

---

$$\begin{aligned}\phi_y - \phi_x &= kd\Delta n \\ \begin{pmatrix} e^{i\phi_x} \cos^2 \theta + e^{i\phi_y} \sin^2 \theta & (e^{i\phi_x} - e^{i\phi_y}) \cos \theta \sin \theta \\ (e^{i\phi_x} - e^{i\phi_y}) \cos \theta \sin \theta & e^{i\phi_x} \sin^2 \theta + e^{i\phi_y} \cos^2 \theta \end{pmatrix} & (1) \\ &= \begin{pmatrix} e^{i\phi_x} \cos^2 \theta + e^{i\phi_y} \sin^2 \theta \\ (e^{i\phi_x} - e^{i\phi_y}) \cos \theta \sin \theta \end{pmatrix} \\ &= e^{i\phi_x} \begin{pmatrix} \cos^2 \theta + (\cos(kd\Delta n) + i \sin(kd\Delta n)) \sin^2 \theta \\ (1 - (\cos(kd\Delta n) + i \sin(kd\Delta n))) \cos \theta \sin \theta \end{pmatrix} \\ &= e^{i\phi_x} \left( \begin{pmatrix} \cos^2 \theta + (\cos(kd\Delta n)) \sin^2 \theta \\ (1 - \cos(kd\Delta n)) \cos \theta \sin \theta \end{pmatrix} + ie^{i\phi_x} \begin{pmatrix} \sin(kd\Delta n) \sin^2 \theta \\ -\sin(kd\Delta n) \cos \theta \sin \theta \end{pmatrix} \right) \\ &= e^{i\phi_x} \left( \begin{pmatrix} \cos^2 \theta + (\cos(kd\Delta n)) \sin^2 \theta \\ (1 - \cos(kd\Delta n)) \cos \theta \sin \theta \end{pmatrix} + i \sin(kd\Delta n) \sin \theta e^{i\phi_x} \begin{pmatrix} \sin \theta \\ -\cos \theta \end{pmatrix} \right)\end{aligned}$$

# Length dependence of Birefringence and Optical Activity

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$$\theta = (n_R - n_L) \frac{\pi l}{\lambda}$$

$$\begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 1 \\ -i \end{bmatrix} + \frac{1}{2} \begin{bmatrix} 1 \\ i \end{bmatrix}$$

$$\frac{1}{2} \begin{bmatrix} 1 \\ -i \end{bmatrix} e^{ik_R l} + \frac{1}{2} \begin{bmatrix} 1 \\ i \end{bmatrix} e^{ik_L l}$$

$$\frac{1}{2} e^{i(k_R+k_L)l/2} \left( \begin{bmatrix} 1 \\ -i \end{bmatrix} e^{i(k_R-k_L)l/2} + \begin{bmatrix} 1 \\ i \end{bmatrix} e^{-i(k_R-k_L)l/2} \right)$$

$$= \frac{1}{2} e^{i(k_R+k_L)l/2} \left( \begin{bmatrix} 1 \\ -i \end{bmatrix} e^{i\theta} + \begin{bmatrix} 1 \\ i \end{bmatrix} e^{-i\theta} \right)$$

$$= e^{i(k_R+k_L)l/2} \frac{1}{2} \begin{bmatrix} e^{i\theta} + e^{-i\theta} \\ i(e^{i\theta} - e^{-i\theta}) \end{bmatrix}$$

$$= e^{i(k_R+k_L)l/2} \frac{1}{2} \begin{bmatrix} \cos\theta \\ \sin\theta \end{bmatrix}$$

Optical Activity from Achiral Components?

## Gibbs's suggestion

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### ON DOUBLE REFRACTION IN PERFECTLY TRANSPARENT MEDIA WHICH EXHIBIT THE PHENOMENA OF CIRCULAR POLARIZATION.

[*American Journal of Science*, ser. 3, vol. XXIII, pp. 460-476, June, 1882.]

With respect to the quantity  $\phi$ , and the surfaces which determine it, the following principle is of fundamental importance. If one body is identical in its internal structure with the image by reflection of another, the values of  $\phi$  in corresponding lines in the two bodies will be numerically equal but have opposite signs.\*

It follows that if a body is identical in internal structure with its own image by reflection, the value of  $\phi$  (if not zero for all directions) must be positive for some directions and negative for others. Moreover, the above described surface by which  $\phi$  is represented must consist of two conjugate hyperboloids, of which one is identical in form with the image by reflection of the other. This requires that the hyperboloids shall be right cylinders with conjugate rectangular hyperbolas for bases. A crystal characterized by such properties will belong to the tetragonal system. Since  $\phi=0$  for the optic axis, it would be difficult to distinguish a case of this kind from an ordinary uniaxial crystal, unless the ellipsoid (24) should approach very closely to a sphere.†

crystal family	crystal system	point group / crystal class	Schönflies	Hermann-Mauguin	Orbifold	Coxeter	Point symmetry	Order	Group structure
triclinic		triclinic-pedial	C <sub>1</sub>	1	11	[ ] <sup>+</sup>	enantiomorphic polar	1	trivial
		triclinic-pinacoidal	C <sub>i</sub>	T	1x	[2,1 <sup>+</sup> ]	centrosymmetric	2	cyclic
monoclinic		monoclinic-sphenoidal	C <sub>2</sub>	2	22	[2,2] <sup>+</sup>	enantiomorphic polar	2	cyclic
		monoclinic-domatic	C <sub>s</sub>	m	*11	[ ]	polar	2	cyclic
		monoclinic-prismatic	C <sub>2h</sub>	2/m	2*	[2,2 <sup>+</sup> ]	centrosymmetric	4	2×cyclic
orthorhombic		orthorhombic-sphenoidal	D <sub>2</sub>	222	222	[2,2] <sup>+</sup>	enantiomorphic	4	dihedral
		orthorhombic-pyramidal	C <sub>2v</sub>	mm2	*22	[2]	polar	4	dihedral
		orthorhombic-bipyramidal	D <sub>2h</sub>	mmm	*222	[2,2]	centrosymmetric	8	2×dihedral
tetragonal		tetragonal-pyramidal	C <sub>4</sub>	4	44	[4] <sup>+</sup>	enantiomorphic polar	4	cyclic
		tetragonal-disphenoidal	S <sub>4</sub>	4	2x	[2 <sup>+</sup> ,2]	non-centrosymmetric	4	cyclic
		tetragonal-dipyramidal	C <sub>4h</sub>	4/m	4*	[2,4 <sup>+</sup> ]	centrosymmetric	8	2×cyclic
		tetragonal-trapezoidal	D <sub>4</sub>	422	422	[2,4] <sup>+</sup>	enantiomorphic	8	dihedral
		ditetragonal-pyramidal	C <sub>4v</sub>	4mm	*44	[4]	polar	8	dihedral
		tetragonal-scalenoidal	D <sub>2d</sub>	42m or 4m2	2*2	[2 <sup>+</sup> ,4]	non-centrosymmetric	8	dihedral
		ditetragonal-dipyramidal	D <sub>4h</sub>	4/mmm	*422	[2,4]	centrosymmetric	16	2×dihedral

	trigonal-pyramidal	$C_3$	3	33	$[3]^+$	enantiomeric polar	3	cyclic	
	rhombohedral	$S_6(C_{3i})$	3	3x	$[2^+,3^+]$	centrosymmetric	6	cyclic	
trigonal	trigonal-trapezoidal	$D_3$	32 or 321 or 312	322	$[3,2]^+$	enantiomeric	6	dihedral	
	ditrigonal-pyramidal	$C_{3v}$	3m or 3m1 or 31m	*33	[3]	polar	6	dihedral	
	ditrigonal-scalahedral	$D_{3d}$	3m or 3m1 or 31m	2*3	$[2^+,6]$	centrosymmetric	12	dihedral	
hexagonal	hexagonal-pyramidal	$C_6$	6	66	$[6]^+$	enantiomeric polar	6	cyclic	
	hexagonal	trigonal-dipyramidal	$C_{3h}$	6	3*	$[2,3^+]$	non-centrosymmetric	6	cyclic
		hexagonal-dipyramidal	$C_{6h}$	6/m	6*	$[2,6^+]$	centrosymmetric	12	2×cyclic
		hexagonal-trapezoidal	$D_6$	622	622	$[2,6]^+$	enantiomeric	12	dihedral
		dihexagonal-pyramidal	$C_{6v}$	6mm	*66	[6]	polar	12	dihedral
		ditrigonal-dipyramidal	$D_{3h}$	6m2 or 62m	*322	[2,3]	non-centrosymmetric	12	dihedral
		dihexagonal-dipyramidal	$D_{6h}$	6/mmm	*622	[2,6]	centrosymmetric	24	2×dihedral
cubic	tetrahedral	T	23	332	$[3,3]^+$	enantiomeric	12	alternating	
	hextetrahedral	$T_d$	43m	*332	[3,3]	non-centrosymmetric	24	symmetric	
	diploidal	$T_h$	m3	3*2	$[3^+,4]$	centrosymmetric	24	2×alternating	
	gyroidal	O	432	432	$[4,3]^+$	enantiomeric	24	symmetric	
	hexoctahedral	$O_h$	m3m	*432	[4,3]	centrosymmetric	48	2×symmetric	

# Measurement of Optical Activity in Achiral Crystal

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*Acta Cryst.* (1968). A 24, 676

## Optical Activity in a Non-enantiomorphous Crystal: AgGaS<sub>2</sub>

BY M. V. HOBDEN

*Royal Radar Establishment, Malvern, Worcestershire, England*

(Received 19 April 1968)

There are no symmetry properties in the theory of optical activity that forbid optical activity in the four non-enantiomorphous crystal classes  $m$ ,  $mm2$ ,  $4$  and  $\bar{4}2m$ , but the existence of such a phenomenon has not, until now, been experimentally verified. This work describes the first positive observation of optical activity in a non-enantiomorphous crystal, silver thiogallate (AgGaS<sub>2</sub>). Measurements of the refractive indices of this crystal show that it is accidentally optically isotropic at 4974 Å, although it is of class  $\bar{4}2m$ . At this wavelength the rotation of the plane of polarization has been measured for propagation along both diad axes. The optical rotatory power is 522 deg.mm<sup>-1</sup>, the sense of rotation being opposite for the two diad axes. There was no rotation along the  $c$  axis. These observations substantiate the theory of optical activity and show that there are no unsuspected conditions forbidding optical activity in these classes; the previous absence of experimental verification of this phenomenon has been due to the lack of crystals with suitable optical properties.

# Measurement of Optical Activity in Achiral Crystal

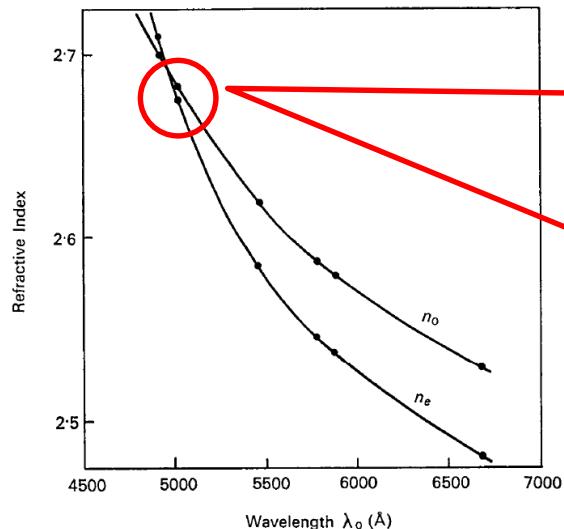


Fig. 1. The refractive indices of  $\text{AgGaS}_2$  at  $20^\circ\text{C}$ .

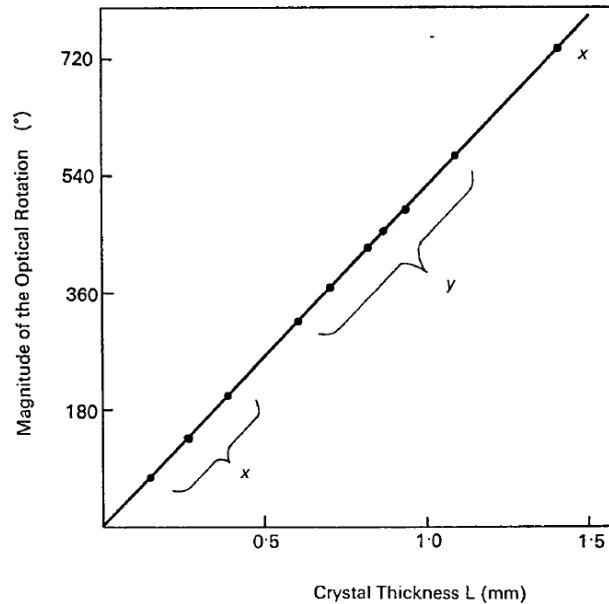


Fig. 2. Magnitude of the optical rotation in degrees for various thicknesses of  $\text{AgGaS}_2$  in the form of polished plates. Data points  $x$  refer to specimens cut perpendicular to one diad axis and  $y$  to those cut perpendicular to the other diad axis. The rotation for  $x$  and  $y$  specimens was of the opposite hand.

# Measurement of Optical Activity in Achiral Crystal

**Table 1:** Measured optical rotation of achiral crystals.

Formula	Point group	Space group	Ref.
AgGaS <sub>2</sub>	D <sub>2d</sub>	P42 <sub>1</sub> c	[48, 49, 53, 54]
BaMnF <sub>4</sub>	C <sub>2v</sub>	A2 <sub>1</sub> am	[55]
Ba <sub>2</sub> Si <sub>2</sub> TiO <sub>8</sub>	C <sub>2v</sub>	P2bm	[56]
C(CH <sub>2</sub> OH) <sub>4</sub>	S <sub>4</sub>	I $\bar{4}$	[57]
CdGa <sub>2</sub> S <sub>4</sub>	S <sub>4</sub>	I $\bar{4}$	[51]
Co <sub>3</sub> B <sub>7</sub> O <sub>13</sub> I	C <sub>2v</sub>	Pca2 <sub>1</sub>	[58]
CsD <sub>2</sub> AsO <sub>4</sub> , D/H = 0.6	D <sub>2d</sub>	I $\bar{4}2d$	[59]
CsH <sub>2</sub> AsO <sub>4</sub>	D <sub>2d</sub>	I $\bar{4}2d$	[58]
CsLiB <sub>6</sub> O <sub>10</sub>	D <sub>2d</sub>	I $\bar{4}2d$	[60]
Cu <sub>3</sub> B <sub>7</sub> O <sub>13</sub> Cl	C <sub>2v</sub>	Pna2 <sub>1</sub>	[57]
Fe <sub>3</sub> B <sub>7</sub> O <sub>13</sub> I	C <sub>2v</sub>	Pca2 <sub>1</sub>	[61]
Gd <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	C <sub>2v</sub>	Pba2	[62]
K <sub>2</sub> ZnCl <sub>4</sub> (300 K)	C <sub>2v</sub>	Pna2 <sub>1</sub>	[63]
K <sub>2</sub> ZnCl <sub>4</sub> (50 K)	Cs	A1a1	[63]
KD <sub>2</sub> PO <sub>4</sub>	D <sub>2d</sub>	I $\bar{4}2d$	[58]
KH <sub>2</sub> PO <sub>4</sub>	D <sub>2d</sub>	I $\bar{4}2d$	[64–67]
KTiOPO <sub>4</sub>	C <sub>2v</sub>	Pna2 <sub>1</sub>	[68]
LiH(SeO <sub>3</sub> ) <sub>2</sub>	C <sub>s</sub>	Pn	[47]
NaNO <sub>2</sub>	C <sub>2v</sub>	Imm2	[46]
Na <sub>2</sub> ZnGeO <sub>4</sub>	C <sub>s</sub>	Pn	[69]
(NH <sub>3</sub> (CH <sub>3</sub> )) <sub>5</sub> (Bi <sub>2</sub> Br <sub>11</sub> )	C <sub>2v</sub>	Pca2 <sub>1</sub>	[70]
NH <sub>4</sub> H <sub>2</sub> AsO <sub>4</sub>	D <sub>2d</sub>	I $\bar{4}2d$	[71]
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	D <sub>2d</sub>	I $\bar{4}2d$	[59, 72]
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	C <sub>2v</sub>	Pmcn	[73]
RbH <sub>2</sub> PO <sub>4</sub>	D <sub>2d</sub>	I $\bar{4}2d$	[65, 74]
RbTiOAsO <sub>4</sub>	C <sub>2v</sub>	Pna2 <sub>1</sub>	[75]
RbTiOPO <sub>4</sub>	C <sub>2v</sub>	Pna2 <sub>1</sub>	[76]
Sn(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	D <sub>2d</sub>	I $\bar{4}2d$	[77]