

Structure and Absolute Optical Chirality of Zinc Selenate Hexahydrate

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Abstract

The crystal structure and absolute optical chirality of $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$ ($M_r = 316.42$) have been determined. For a crystal that was found to be optically laevo over the wavelength range 0.3655 to 0.6328 μm , the space group was determined to be $P4_12_12$ (D_4^+), with $a = 6.947$ (1), $c = 18.592$ (1) \AA , $V = 897.3$ (3) \AA^3 , $Z = 4$, $D_m = 2.343$ (2), $D_x = 2.342$ Mg m^{-3} , $\text{Mo K}\alpha$, $\lambda = 0.71069$ \AA , $\mu = 6.85$ mm^{-1} , $F(000) = 624$, $T = 297$ K. The structure was refined to $R = 0.0216$ and $wR = 0.0272$ for 688 unique reflections. The optical rotatory dispersion has been determined and the relationship between optical rotation and structural chirality is compared with earlier work on the related compound $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$. The refractive indices and rotatory power are calculated by the program of Devarajan & Glazer [*Acta Cryst.* (1986), **A42**, 560–569]. It is shown that the calculated anisotropic polarizability ellipsoids are roughly perpendicular to the thermal ellipsoids of the O atoms.

Introduction

Recently, Stadnicka, Glazer & Koralewski (1987), hereafter referred to as SGK, determined the absolute chirality of the optically active crystal $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$. The optical rotatory dispersion (ORD) of this compound is anomalous in that it shows a number of changes in sign with wavelength, but SGK were able to demonstrate that once the contributions from $d-d$ transitions in the $\text{Ni}(\text{H}_2\text{O})^{2+}$ moiety are subtracted the resulting ORD curve, which is due essentially to the O atoms, is normal. It was further shown that the sign of the optical rotation due to the O atoms was consistent with the theory of Glazer & Stadnicka (1986) and that detailed calculations using the program of Devarajan & Glazer (1986) gave a reasonably good fit to the observed rotation. These calculations also demonstrated that the water O atoms played a more significant role in

the optical rotation than those belonging to the sulfate groups.

In order to underline these observations, we now consider the isostructural compound $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$, where no $d-d$ transitions occur. It was shown by Kato, Ban & Tsujikawa (1972) that crystals of this material are optically active with a normal ORD over the visible range, as expected. Gailey, Giles & Palmer (1973) determined the structure and absolute chirality of $\text{Zn}_{0.62}\text{Co}_{0.38}\text{SeO}_4 \cdot 6\text{H}_2\text{O}$ (they used a doped crystal in order to assess the importance of the transition-metal ions in the circular dichroism associated with the anomalous ORD). The structure determination was carried out with photographic methods and little structural data were reported. Palmer & Giles (1978) republished the structure determination in more detail, and admitted that the assignment of absolute optical chirality (relationship between optical rotation and space group) had been incorrectly reported by Gailey *et al.* (1973) because of an indexing error. Finally, Richardson & Hilmes (1975) discussed the theory of optical activity (at least as far as the transition-metal ions are concerned) in a Cu-doped crystal. In the present paper, we concentrate on the pure zinc selenate hexahydrate.

Crystal preparation and optical measurements

Zinc selenate hexahydrate was prepared from basic zinc carbonate (BDH, UK, for chromatographic analysis) and selenic acid (Ventron, Federal Republic of Germany) in aqueous solution and recrystallized five times. On slow evaporation at about 291 K, colourless bipyramidal crystals of good optical quality and several millimetres across were obtained. The hydrogen content was checked by chemical analysis and corresponded to six molecules of water per formula unit. The density of the crystals was found by flotation in a mixture of bromoform and xylene to be 2.343 (2) Mg m^{-3} . Fig. 1 shows the crystal morphology.

Five (001) slices of various thicknesses (in the range 0.637 to 6.705 mm) were cut and polished for measurement of the ORD at room temperature. A Polamat spectropolarimeter (Zeiss Jena, Federal Republic of Germany) and the modulation method of Habryło & Koralewski (1981) were used to measure the rotation angle of plane-polarized light passing through the crystals. An Hg lamp with interference filters was used as the light source for the spectropolarimeter and Ar-ion and He/Ne lasers were used for the modulation method. The sign of rotation was checked by rotation of the analyser and by observation of Airy's spiral, and was found to be negative (laevorotatory crystal) in all the slices.

Structure determination

A piece of the crystal of $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$ used for the ORD measurements was cut approximately in the shape of a parallelepiped with {001} and {110} faces, measuring 0.07 (1) mm between (001) and (00 $\bar{1}$), 0.11 (1) mm between (110) and ($\bar{1}\bar{1}0$), and 0.11 (1) mm between (1 $\bar{1}0$) and ($\bar{1}10$). The crystal was coated in silicone oil to limit evaporation of water. X-ray measurements were made on the Enraf-Nonius CAD-4F-11 diffractometer at the Polish Academy of Sciences (Warsaw, Poland) using graphite-mo-chromated Mo $K\alpha$ radiation. The lattice parameters were obtained by least-squares fit using 25 reflections with $11 < \theta < 28^\circ$. The intensity data were collected in the range $0 \leq h \leq k$, $0 \leq k \leq 8$ and $0 \leq l \leq 23$ interleaved with their Friedel equivalents $\bar{h}\bar{k}\bar{l}$ up to $\theta = 27^\circ$ in the θ - 2θ scan mode, with the scan width given by $(0.70 + 0.35 \tan \theta)^\circ$. Two intensity control reflections were monitored hourly and showed no systematic changes. The average variation was less than 1.2%. Because of the tendency for the crystal to lose water, all measurements had to be performed relatively quickly. From 1312 measured reflections, 371 (including 42

systematically absent reflections) had $I \leq \sigma(I)$ and so were removed. The remaining 941 reflections were corrected for Lp factors and absorption (maximum and minimum transmission factors were 0.6323 and 0.5010, respectively) using the *SHELX76* program (Sheldrick, 1976). Symmetrically equivalent reflections ($hk0$ and $\bar{h}\bar{k}0$; $0kl$ and $0\bar{k}\bar{l}$; hhl and $\bar{h}\bar{h}\bar{l}$) were then averaged ($R_{\text{int}} = 0.0117$, to be compared with $R_{\text{int}} = 0.0197$ when merged to include Friedel opposites) to give 722 unique mean values of $|F(hkl)|$. Refinement of 688 values of $|F(hkl)| > 3\sigma$ was carried out with the *SHELX76* program in both enantiomorphic space groups, incorporating neutral atomic scattering factors and anomalous-scattering factors taken from *International Tables for X-ray Crystallography* (1974).

The initial atomic coordinates for non-H atoms were taken from the α - $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ structure determination by SGK. Refinement parameters, 83 altogether, included the scale factor, the crystal size, isotropic extinction and the g term in the weighting scheme used in *SHELX76*. H atoms were located on difference Fourier maps. The temperature factors were refined anisotropically for non-H atoms and isotropically for H atoms. In the final stage of refinement the difference Fourier maps showed electron density of between $+0.19$ and $-0.35 \text{ e } \text{\AA}^{-3}$. For space group $P4_12_12$ the final agreement factors were $R = 0.0216$, $wR = 0.0272$ with weights given by $w = 1.0871/(\sigma^2 + 0.000613F_o^2)$; goodness-of-fit parameter $S = 0.92$; average $\Delta/\sigma < 0.02$ for non-H atoms and < 0.13 for H atoms (the maximum values were 0.05 and 0.3, respectively). The crystal size and isotropic extinction parameters (*SHELX76*) converged to 1.010 (2) and 0.0029 (1). Refinement with the sign of f'' changed (equivalent to $P4_32_12$ with atomic coordinates inverted) gave $R = 0.0339$, $wR = 0.0454$. Recalculation of the structure factors for models $P4_12_12$ ($\bar{x}\bar{y}\bar{z}$) and $P4_32_12$ (xyz) gave R about 0.13 and wR about 0.32. This clearly demonstrates that our crystal is the $P4_12_12$ (xyz) enantiomorph. The final atomic coordinates and temperature factors are given in Table 1 and important interatomic distances and angles (to compare with α - $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) in Table 2.*

The structure (Fig. 2) is very similar to that of α - $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (see SGK for details). The average Zn—O distance [2.090 (3) \AA] is 0.039 \AA longer than the corresponding Ni—O distance, in agreement with the ionic radii published by Shannon (1976). The average Se—O distance is 1.636 (2) \AA , 0.16 \AA longer than the corresponding S—O distance, and this also agrees with the difference in ionic radii of Se^{6+} and S^{6+} (Shannon, 1976). The average value for Se—O and

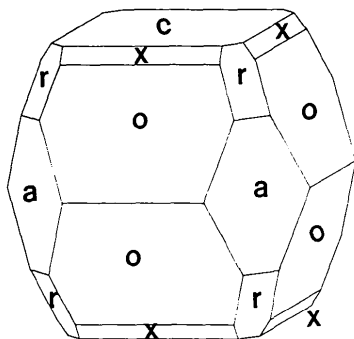


Fig. 1. Habit of a typical $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$ crystal. The faces are marked according to Groth (1908), but with his indices transformed by the matrix $\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ in order to conform to a primitive tetragonal lattice: a {110}; c {001}; o {011}; x {012}; r {112}.

* A list of structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44794 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates and thermal parameters with *e.s.d.*'s in parentheses

$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots)]$, where U_{ij} are in \AA^2 . For H atoms, the anisotropic U is given.

	Site	Point symmetry	x	y	z
Zn	4 (a)	..2	0.21724 (6)	0.21724 (6)	0.00000
Se	4 (a)	..2	0.71562 (5)	0.71562 (5)	0.00000
O1	8 (b)	1	0.1801 (4)	-0.0386 (4)	0.0526 (2)
O2	8 (b)	1	0.4739 (4)	0.2523 (4)	0.0570 (2)
O3	8 (b)	1	0.0735 (4)	0.3628 (4)	0.0859 (1)
O4	8 (b)	1	0.6179 (4)	0.6222 (4)	0.0722 (1)
O5	8 (b)	1	0.9475 (3)	0.6757 (4)	0.0028 (2)
H11	8 (b)	1	0.096 (2)	-0.095 (2)	0.045 (2)
H12	8 (b)	1	0.231 (2)	-0.058 (2)	0.088 (2)
H21	8 (b)	1	0.564 (2)	0.166 (2)	0.051 (2)
H22	8 (b)	1	0.510 (2)	0.348 (2)	0.062 (2)
H31	8 (b)	1	0.010 (2)	0.440 (2)	0.077 (2)
H32	8 (b)	1	0.006 (2)	0.279 (2)	0.125 (2)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zn	0.0187 (2)	0.0187 (2)	0.0193 (3)	0.0007 (2)	-0.0007 (2)	-0.0021 (2)
Se	0.0157 (2)	0.0157 (2)	0.0225 (3)	-0.0013 (2)	0.0013 (2)	0.0002 (2)
O1	0.034 (2)	0.030 (1)	0.036 (1)	0.018 (1)	-0.015 (1)	-0.011 (1)
O2	0.019 (1)	0.022 (1)	0.035 (1)	-0.005 (1)	-0.003 (1)	-0.001 (1)
O3	0.025 (1)	0.024 (1)	0.026 (1)	-0.001 (1)	0.002 (1)	0.003 (1)
O4	0.048 (1)	0.023 (1)	0.030 (1)	-0.002 (1)	0.014 (1)	-0.006 (1)
O5	0.017 (1)	0.027 (1)	0.043 (1)	-0.006 (1)	-0.004 (1)	0.005 (1)
H11	0.048 (2)					
H12	0.046 (2)					
H21	0.047 (2)					
H22	0.047 (2)					
H31	0.050 (2)					
H32	0.061 (2)					

Table 2. Important interatomic distances and angles

(a) Bond lengths (\AA) and angles ($^\circ$)

Zn-O1	2.045 (3)	O1-H11	0.72 (1)
Zn-O2	2.088 (3)	O1-H12	0.75 (2)
Zn-O3	2.138 (2)	O2-H21	0.88 (1)
		O2-H22	0.72 (1)
Se-O4	1.637 (2)	O3-H31	0.71 (1)
Se-O5	1.635 (2)	O3-H32	1.04 (2)
O1-Zn-O2	88.1 (1)	O4-Se-O5	108.4 (2)
O1-Zn-O3	89.7 (1)	O4-Se-O4 ⁱ	110.1 (2)
O1-Zn-O1 ⁱ	90.6 (2)	O4-Se-O5 ⁱ	110.3 (2)
O1-Zn-O3 ⁱ	90.6 (2)	O5-Se-O5 ⁱ	109.6 (2)
O2-Zn-O3	88.0 (1)		
O2-Zn-O2 ⁱ	93.3 (1)	H11-O1-H12	116 (2)
O2-Zn-O3 ⁱ	91.7 (2)	H21-O2-H22	114 (1)
O1-Zn-O2 ⁱ	178.9 (1)	H31-O3-H32	107 (2)
O3-Zn-O3 ⁱ	179.5 (1)		

(b) Geometry of hydrogen bonding

D-H...A	H...A (\AA)	D...A (\AA)	DHA ($^\circ$)
O1-H11...O5 ⁱⁱ	2.06 (2)	2.722 (4)	155 (2)
O1-H12...O3 ^v	2.04 (2)	2.773 (5)	164 (2)
O2-H21...O5 ⁱⁱⁱ	1.97 (2)	2.772 (5)	151 (2)
O2-H22...O4	2.06 (1)	2.772 (4)	178 (3)
O3-H31...O5 ^{iv}	2.19 (2)	2.808 (4)	146 (3)
O3-H32...O4 ^{vi}	1.71 (2)	2.735 (5)	170 (2)

(c) Non-bonding distances (\AA) less than 3.200 \AA

O1-O2	2.873 (4)	O3-O2 ⁱ	3.032 (5)
O1-O3	2.950 (4)	O2-O1 ⁱⁱ	3.173 (5)
O2-O3	2.935 (4)	O4-O5	2.654 (4)
O1-O1 ⁱ	2.907 (5)	O4-O4 ⁱ	2.683 (5)
O3-O1 ⁱ	2.975 (5)	O5-O4 ⁱ	2.685 (5)
O2-O2 ⁱ	3.038 (6)	O5-O5 ⁱ	2.672 (5)

Symmetry code: (i) $y, x, -z$; (ii) $-1+x, -1+y, z$; (iii) $y, -1+x, -z$; (iv) $-1+x, y, z$; (v) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (vi) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

average valence angle of 109.6° are very close to those obtained for other selenates, for instance: Rb_2SeO_4 , 1.640 \AA and 109.7° (Takahashi, Onodera & Shiozaki,

1987); SrSeO_4 , 1.647 \AA and 109.5° (Prévost-Czeskleba & Endres, 1984); $\text{CdSeO}_4 \cdot \text{H}_2\text{O}$, 1.639 \AA and 109.5° (Stälhandske, 1981); $\text{HgSeO}_4 \cdot \text{H}_2\text{O}$, 1.641 \AA and 109.5° (Stälhandske, 1978).

The water O1, O2 and O3 atoms form distorted octahedra around the Zn^{2+} ions, with O-O contacts between 2.873 (4) and 3.038 (6) \AA [2.829 (2) and 2.982 (2) \AA , respectively, in the nickel compound]. Similarly, the selenate O4 and O5 atoms, which form slightly distorted tetrahedra around Se^{6+} , have O-O contacts between 2.654 (4) and 2.685 (5) \AA , compared with 2.404 (2) and 2.414 (2) \AA .

The hydrogen-bond schemes are closely similar in the two compounds - all H atoms are involved in H bonding (see Table 2c). O1...O3 and O3...O5 are significantly shorter in $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$, and this probably arises from a competition between Zn-O interactions and H bonding. Water molecules $W1$ (H11-O1-H12) and $W2$ (H21-O2-H22) are coordinated to Zn^{2+} by one lone-pair orbital (with the angles between Zn-O and the water-molecule planes being 44.7 and 34.7° for $W1$ and $W2$, respectively) and they form two H-bonds each acting as a donor. Thus they should be classified according to Ferraris & Franchini-Angela (1972) as class 1'(J). In $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (SGK) and $\text{NiSO}_4 \cdot 6\text{D}_2\text{O}$, $W1$ is in class 1(D) with $W2$ in class 1'(J). The third water $W3$ (H31-O3-H32) is the donor of two H bonds; in addition it accepts one H bond from $W1$ (O3...H12 = 2.04 \AA) and it is coordinated to Zn^{2+} by the remaining lone-pair orbital (Zn-O3 = 2.138 \AA). It is therefore in class 2(H).

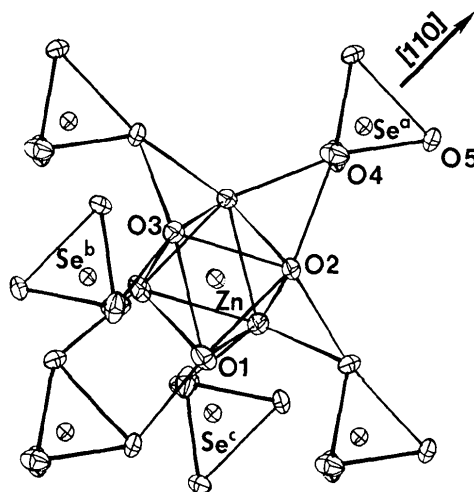


Fig. 2. (001) projection of the $\text{Zn}(\text{OH}_2)_6^{2+}$ group, including thermal ellipsoids drawn at the 75% probability level, with the nearest selenate groups connected by hydrogen bonds. The H atoms have been omitted from the drawing. Fractional heights along c for the atoms labelled in the figure are: Zn, 0.00; Se^a , 0.00; Se^b , 0.25; Se^c , -0.25; O1, 0.0526; O2, 0.0569; O3, 0.0858; O4, 0.0722; O5, 0.0029.

Discussion

Fig. 3 shows the ORD curve obtained along [001] together with the equivalent curve produced by SGK for α -NiSO₄·6H₂O, once the contributions from the $d-d$ transitions in the Ni²⁺ ion had been removed. The ZnSeO₄·6H₂O data were fitted to a Drude-type analytical expression:

$$\rho = 0.7530/(\lambda^2 - \lambda_0^2) - 0.0720,$$

where λ is in μm , ρ is in $^\circ\text{mm}^{-1}$ and $\lambda_0 = 0.1541 \mu\text{m}$. Our ORD curve is similar in shape to that of Kato, Ban & Tsujikawa (1972), although it is displaced about 7% higher in ρ . It can be seen that, nevertheless, it is similar to the α -NiSO₄·6H₂O ORD curve. Because the range of ORD measurements does not extend into the UV, the extrapolated curve above about 0.0159 cm^{-1} (below $0.63 \mu\text{m}$) is likely to be inaccurate. Therefore no significance should be placed on the way in which the ZnSeO₄·6H₂O curve crosses that for α -NiSO₄·6H₂O at about 0.037 cm^{-1} ($0.27 \mu\text{m}$). On the other hand, below 0.037 cm^{-1} the fact that the ZnSeO₄·6H₂O curve lies above that for the nickel compound agrees with the observation that the absorption edge of the former compound (Kato, Ban & Tsujikawa, 1972) appears at a smaller wave number (longer wavelength) than that for the latter (SGK).

As with the α -NiSO₄·6H₂O work, in order to understand the optical activity, we consider the most polarizable atoms, namely the O atoms. The relative bond distances show that the Se—O bonds are stronger than the Zn—O bonds, and so O1, O2 and O3 (the water O atoms) will have larger electronic polarizabilities than O4 and O5 (the selenate O atoms).

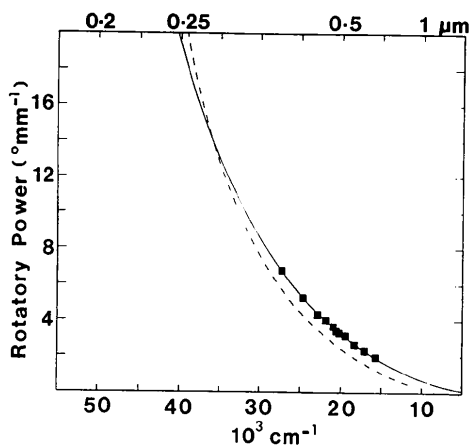


Fig. 3. Magnitude of ORD of ZnSeO₄·6H₂O crystal. The points are an average of the experimental measurements on several crystals (typical error about 3%), and the continuous curve is the Drude-type analytical fit (see text). The dashed curve is for the isostructural compound α -NiSO₄·6H₂O after removal of the contributions from $d-d$ transitions in the Ni ion, according to equation (2) of Stadnicka, Glazer & Koralewski (1987).

Therefore, they should be more important in determining the optical rotatory power. The O1 and O3 atoms, in particular, form a right-hand helix, RS2/8 in the notation of Glazer & Stadnicka (1986), and so it has the same chirality as the sense of rotation of the plane-polarized light (Fig. 4).

To quantify this, we have used the Devarajan & Glazer (1986) program to calculate refractive indices and optical rotatory power. Table 3 summarizes the various attempts to get close to the observed values.

When using isotropic polarizability volumes as starting parameters for the program, there are seven independent atoms to consider, and so it is not possible to define uniquely the polarizabilities in calculating the optical quantities. Nevertheless, as a result of many calculations, using many combinations of polarizability values, we can infer certain constraints. The water O atoms must always be assigned larger polarizability volumes than the selenate O atoms to get the correct sign of rotatory power. On the other hand, the calculated birefringence then has the wrong sign, although, nevertheless, the average refractive index agrees well with experiment. We have tried some calculations with the polarizability of O2 less than O1 and O3 and found that this leads to a more positive birefringence and a more negative ρ . This shows that the contribution from O2 is opposite to that from the RS2/8 helix of O1 and O3 atoms. Addition of small contributions from Zn²⁺ makes a significant improvement to the value of ρ , but with little effect on the birefringence. Addition of Se⁶⁺ does not seriously affect either. We would normally not consider such a small discrepancy in the computed birefringences to be significant, given the approximations inherent in the point-dipole model used in the computer program. However, it is worth recalling that the theory allows anisotropic polarizabilities to be used as starting values. Consequently, we have tried some runs using anisotropic polarizability volumes in which we put $\alpha_{33} < \alpha_{11} = \alpha_{22}$ by about 5 to 8%. This is compatible with the fact that the structure consists of (001) layers of alternating oxygen octahedra and tetrahedra (see Fig.

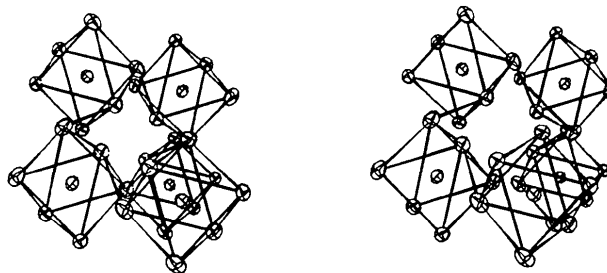


Fig. 4. Stereoprojection of the region around the 4_1 axis through $(0, \frac{1}{2}, z)$. O1 and O3 lie on an RS2/8 helix consisting of alternating O3—O1 contacts (2.978 Å) and O1...O3 hydrogen bonds (2.772 Å).

Table 3. Results of calculations of refractive indices and optical rotatory power along [001] at $\lambda = 0.4861 \mu\text{m}$ in $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$

The calculations were made with the program of Devarajan & Glazer (1986). The order in the table is according to the ratio (R) of O1, O2, O3 to O4, O5 polarizability volumes.

Model No.	$R(\%)$	Polarizability volumes (\AA^3)			Zn/Se*	n_o	n_e	Δn	$\rho(^{\circ}\text{mm}^{-1})$
		O1 O2 O3	O4 O5						
Isotropic									
1	0.60	1.290	2.150	—	1.546	1.526	-0.020	+5.4	
2	1.00	1.638	1.638	—	1.536	1.522	-0.014	+2.0	
3	1.38	1.842	1.331	—	1.531	1.530	-0.001	-0.8	
4	1.42	1.856	1.310	—	1.531	1.531	0.000	-0.7	
5	1.67	1.950	1.170	—	1.529	1.537	+0.008	-2.0	
6	1.80	1.992	1.107	—	1.528	1.540	+0.012	-2.4	
7	1.80	1.945	1.080	Zn+Se	1.532	1.546	+0.014	-3.2	
8	1.90	2.017	1.062	—	1.527	1.541	+0.014	-2.5	
9	1.90	1.974	1.039	Zn+Se	1.530	1.547	+0.017	-3.2	
10	2.01	2.050	1.020	—	1.527	1.545	+0.018	-2.8	
11	2.01	2.040	1.015	Se	1.528	1.545	+0.017	-2.5	
12	2.01	2.006	0.998	Zn+Se	1.531	1.550	+0.020	-3.3	
13	2.01	2.015	1.002	Zn	1.530	1.551	+0.021	-3.5	
14	2.50	2.155	0.862	—	1.526	1.556	+0.030	-3.0	
Anisotropic†									
15	1.80	α_{11}	1.986	1.104	Zn+Se	1.543	1.516	-0.027	-3.1
		α_{33}	1.866	1.037					
16	1.90	α_{11}	2.014	1.060	Zn+Se	1.543	1.519	-0.024	-3.2
		α_{33}	1.894	0.996					
17	1.90	α_{11}	2.021	1.064	Zn+Se	1.545	1.514	-0.031	-3.2
		α_{33}	1.880	0.990					
Experimental						1.539‡	1.517‡	-0.022	-3.5§
Estimated errors						(0.001)	(0.001)		(0.1)

* The isotropic polarizability volumes for Zn^{2+} and Se^{6+} were taken to be 0.28 and 0.08 \AA^3 , respectively (Pauling, 1927).

† The polarizability volumes were given the same percentage anisotropy for all atoms; $\alpha_{22} = \alpha_{11}$, $\alpha_{ij} (i \neq j) = 0$.

‡ Estimated from data given in Landolt-Börnstein (1962).

§ Present work.

2b of SGK). As seen in Table 3, we can then obtain excellent agreement with both the observed refractive indices and the birefringence. At the same time, the calculated value of rotatory power is hardly affected.

The program renormalizes the input polarizabilities (whether isotropic or not) and calculates a set of effective anisotropic polarizabilities. In Fig. 5 the (010) projections of part of the structure are given, in which one ZnO_6 helix (through $0, \frac{1}{2}, z$) is shown. In Fig. 5(a) thermal ellipsoids are plotted and in Fig. 5(b) ellipsoids representing the calculated anisotropic polarizabilities. It can be seen that the polarizability ellipsoids of the O atoms tend to line up with the O—O contacts of the $RS2/8$ helix, *i.e.* they are approximately tangential to the helix [according to Glazer & Stadnicka (1986) this means that polarized light will rotate in the *same* sense as the helix]. Moreover, we note that they are approximately perpendicular to the thermal ellipsoids. This relationship has been found in almost all of the other compounds for which polarizability ellipsoids have been calculated and seems to be generally true, as first predicted by Glazer & Stadnicka. It can be quantified by calculating the eigenvalues and eigenvectors for the thermal and polarizability ellipsoids (Table 4). From the relevant eigenvectors of model 15 (the results are almost identical for models 15, 16 and 17), we then find the following:

(1) The angles between the largest thermal and polarizability eigenvalues are

for O1 (eigenvalues 0.0623 \AA^2 and 3.66 \AA^3) 87°

for O2 (eigenvalues 0.0369 \AA^2 and 3.15 \AA^3) 95°

for O5 (eigenvalues 0.0458 \AA^2 and 1.87 \AA^3) 86°,

all close to 90°.

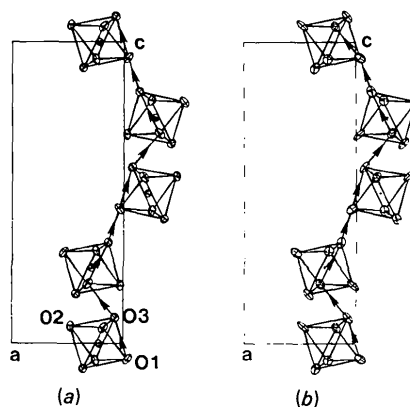


Fig. 5. ZnO_6 octahedra projected on (010). Only one helix of octahedra is shown. Arrows denote the $RS2/8$ helix of alternating O1 and O3. (a) Thermal ellipsoids plotted at 75% probability. (b) Anisotropic polarizability ellipsoids as determined by the Devarajan & Glazer (1986) program for model 15 (Table 3), drawn on arbitrary scale.

Table 4. *Eigenvalues and eigenvectors of thermal and polarizability ellipsoids for O atoms in ZnSeO₄·6H₂O (for model 15 in Table 3)*

Thermal eigenvalues (Å²) and eigenvectors

O1	$\begin{bmatrix} 0.0148 \\ 0.0222 \\ 0.0623 \end{bmatrix}$	$\begin{bmatrix} -0.0967 & 0.7318 & -0.6746 \\ 0.8407 & 0.4228 & 0.3382 \\ 0.5328 & -0.5345 & -0.6562 \end{bmatrix}$
O2	$\begin{bmatrix} 0.0174 \\ 0.0216 \\ 0.0369 \end{bmatrix}$	$\begin{bmatrix} -0.7824 & -0.5562 & -0.2800 \\ 0.6089 & -0.7777 & -0.1566 \\ -0.1307 & -0.2930 & 0.9471 \end{bmatrix}$
O3	$\begin{bmatrix} 0.0210 \\ 0.0254 \\ 0.0276 \end{bmatrix}$	$\begin{bmatrix} 0.6149 & -0.7290 & -0.3007 \\ 0.2141 & 0.5213 & -0.8261 \\ 0.7590 & 0.4436 & 0.4766 \end{bmatrix}$
O4	$\begin{bmatrix} 0.0210 \\ 0.0232 \\ 0.0565 \end{bmatrix}$	$\begin{bmatrix} 0.3900 & 0.8273 & -0.4044 \\ 0.3236 & -0.5343 & -0.7809 \\ 0.8621 & -0.1737 & 0.4761 \end{bmatrix}$
O5	$\begin{bmatrix} 0.0151 \\ 0.0263 \\ 0.0458 \end{bmatrix}$	$\begin{bmatrix} 0.9329 & -0.3575 & 0.0447 \\ -0.3157 & -0.8710 & -0.3764 \\ -0.1735 & -0.3370 & 0.9254 \end{bmatrix}$

Polarizability eigenvalues (Å³) and eigenvectors

O1	$\begin{bmatrix} 2.32 \\ 2.87 \\ 3.66 \end{bmatrix}$	$\begin{bmatrix} 0.6800 & -0.4366 & -0.5890 \\ 0.7328 & 0.3756 & 0.5674 \\ -0.0265 & -0.8175 & 0.5754 \end{bmatrix}$
O2	$\begin{bmatrix} 2.52 \\ 2.96 \\ 3.15 \end{bmatrix}$	$\begin{bmatrix} -0.1461 & -0.4057 & 0.9023 \\ 0.6244 & -0.7452 & -0.2339 \\ -0.7673 & -0.5292 & -0.3622 \end{bmatrix}$
O3	$\begin{bmatrix} 2.60 \\ 2.71 \\ 3.28 \end{bmatrix}$	$\begin{bmatrix} 0.5500 & 0.6965 & -0.4608 \\ -0.8333 & 0.4210 & -0.3582 \\ -0.0555 & 0.5810 & 0.8120 \end{bmatrix}$
O4	$\begin{bmatrix} 1.24 \\ 1.61 \\ 1.72 \end{bmatrix}$	$\begin{bmatrix} 0.6241 & -0.2870 & 0.7268 \\ -0.1069 & 0.8900 & 0.4432 \\ 0.7740 & 0.3543 & -0.5248 \end{bmatrix}$
O5	$\begin{bmatrix} 1.20 \\ 1.66 \\ 1.87 \end{bmatrix}$	$\begin{bmatrix} -0.1408 & -0.1657 & 0.9761 \\ -0.5665 & -0.7951 & -0.2167 \\ 0.8120 & -0.5834 & 0.0180 \end{bmatrix}$

(2) O3 is almost isotropic in its thermal ellipsoid (this is not surprising, since this O atom is involved in three hydrogen bonds (Table 2b) and is also coordinated to Zn) and so the angle cannot be determined.

(3) O4 is rather disc-shaped in its polarizability ellipsoid (eigenvalues 1.61 and 1.72 Å³): we calculate that the direction perpendicular to the disc is only 21° off the direction of the largest thermal eigenvalue (0.0565 Å²).

Given that all the O atoms are on general positions, so that there are no symmetry constraints limiting the directions of the ellipsoids, these results clearly show that anisotropic polarizabilities do tend to be largest in directions where thermal motion is smallest.

Concluding remarks

A link between optical activity and structural chirality (*i.e.* the absolute chirality) in ZnSeO₄·6H₂O has been established, and the close similarity with the more complicated case of α-NiSO₄·6H₂O confirms that the explanation for its optical activity given by SGK is

correct. We have also established a clear relationship between the orientations of polarizability and thermal ellipsoids, just as had been predicted earlier by Glazer & Stadnicka (1986) before any detailed computations had been undertaken. At the same time, this provides further evidence that thermal ellipsoids obtained by X-ray diffraction do have some significance and are not meaningless, as some believe.

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