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## Structure and absolute optical chirality of thulium pyrogermanate crystals

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**Abstract.** The crystal structure and absolute optical chirality of  $\text{Tm}_2\text{Ge}_2\text{O}_7$  ( $M_r = 595.04$ ) have been determined by x-ray diffraction at room temperature. An optically laevorotatory crystal had space group  $P4_12_12$  ( $D_4^1$ ), with  $a = 6.764(2)$ ,  $c = 12.293(2)$  Å,  $V = 562.4(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 7.027$  mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 42.03$  mm<sup>-1</sup>,  $F(000) = 1032$ . The final  $R$ -factors were  $R = 0.0276$  and  $wR = 0.0369$  for 1568 reflections. It is found that  $\text{Tm}^{3+}$  is unusual in being coordinated by seven oxygens. The refractive indices and optical rotatory dispersion have been measured. Using a point dipole polarisability theory it was possible to compute the optical rotatory power, and this was found to be in close agreement with the observed value. It is found that the main contribution to the optical rotation is from the O1, O2 and O3 oxygens, with O3 playing the major role.

### 1. Introduction

In order to extend our program of research into the connection between optical activity and crystal structures of inorganic materials (Glazer and Stadnicka 1986, Stadnicka *et al* 1987, 1988, Swindells and Leal Gonzalez 1988) we consider here a different type of crystal containing rare-earth elements, which are known to influence optical properties severely.

Wanklyn (1973) had earlier grown by flux techniques the rare-earth series of pyrogermanates  $\text{R}_2\text{Ge}_2\text{O}_7$  ( $\text{R} = \text{Tb to Lu}$ ). As these crystals appeared to be highly perfect (Clark *et al* 1980) and clearly showed optical activity, they attracted our interest. Emelchenko *et al* (1975) grew some of them using hydrothermal methods, and some of the physical properties have been reported by Bondar (1979)—refractive indices were given for the  $\text{La}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Y}^{3+}$  (triclinic) and  $\text{Er}^{3+}$  (tetragonal) pyrogermanates. Optical absorption spectra and crystal field parameters were published by Wardzyńska and Wanklyn (1977) for dysprosium and erbium pyrogermanates, and optical studies of the  $\text{Er}^{3+}$  ion were described by Yaeger *et al* (1981).

Hitherto, a few structure determinations have been published:  $\text{Er}_2\text{Ge}_2\text{O}_7$  (Smolin 1970),  $\text{Eu}_2\text{Ge}_2\text{O}_7$  (Chiragov *et al* 1983) and  $\text{Tb}_2\text{Ge}_2\text{O}_7$  (Geller and Gaines 1987). These structures were found to be isomorphous with space group  $P4_12_12$  (or  $P4_32_12$ ), but no absolute optical chirality has been reported. In these compounds, the rare-earth element

is coordinated by seven oxygens, and so we were interested to see if this were true also for  $\text{Tm}_2\text{Ge}_2\text{O}_7$ , especially as in the literature  $\text{Tm}^{3+}$  crystals have only been reported to have 6-, 8- or 9-coordination (for example, see Shannon 1976, Mullica *et al* 1979, Chizhov *et al* 1982, Milligan *et al* 1983, Prout *et al* 1985).

## 2. Crystal preparation and optical measurements

Large, good-quality, pale green crystals of thulium pyrogermanate were obtained by flux growth (Wanklyn 1973). A 0.737 mm thick (001) slice of  $\text{Tm}_2\text{Ge}_2\text{O}_7$  was cut and polished for measurement of the optical rotatory dispersion (ORD) at room temperature. The orientation was checked by observation of optical conoscopic figures, and the ORD was measured by a Polamat spectropolarimeter (Zeiss, Jena) and by the modulation method of Habryło and Koralewski (1981). A mercury lamp with interference filters was used as a light source for the spectropolarimeter, and argon-ion and He/Ne lasers for the modulation method. The sign of rotation was found to be negative (laevorotatory) and this was checked by observation of Airy's spiral.

The average refractive index was measured, and found to be 1.895(6), by the minimum deviation method using a He/Ne laser as light source ( $\lambda = 6328 \text{ \AA}$ ) with the crystal cut and polished to form a prism of angle  $43.2^\circ$ . The birefringence was found by measurement to be  $-0.010$ , using an Ehringhaus compensator for a plate of 1.12 mm thickness cut with the optic axis parallel to the plate. Thus we calculate  $n_\omega = 1.900$  and  $n_\epsilon = 1.890$  (this may be compared with  $n_\omega = 1.876$  and  $n_\epsilon = 1.867$  for  $\text{Er}_2\text{Ge}_2\text{O}_7$  (Bondar 1979)).

## 3. Structure determination

A small piece of laevorotatory crystal of  $\text{Tm}_2\text{Ge}_2\text{O}_7$  was cut approximately in the shape of a parallelepiped with {100} and {001} faces, and measuring 0.11(1) mm between (100) and ( $\bar{1}00$ ), 0.05(1) mm between (010) and ( $0\bar{1}0$ ), and 0.07(1) mm between (001) and ( $00\bar{1}$ ). X-ray measurements were made on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). The lattice parameters  $a = 6.764(2)$  and  $c = 12.293(2) \text{ \AA}$  were obtained by least-squares fitting using 25 reflections with  $7 < \theta < 19^\circ$ . The intensity data were collected up to  $\theta = 40^\circ$  in the  $\theta$ - $2\theta$  scan mode, with the scan width given by  $(0.65 + 0.35 \tan \theta)^\circ$ . Two intensity control reflections were monitored hourly and showed no systematic changes. The average variation was less than 1.5%. A total of 3472 reflections with  $I > \sigma(I)$  were collected in the range  $0 \leq h \leq 8$ ;  $0 \leq k \leq 8$  and  $-22 \leq l \leq +22$  and corrected for  $Lp$ -factors and absorption (maximum and minimum transmission factors were 0.1950 and 0.0748, respectively) using the SHELX76 program. Symmetrically equivalent reflections were then averaged ( $R_{\text{int}} = 0.0434$  to be compared with  $R_{\text{int}} = 0.0633$  without absorption corrections) to give 1608 unique mean values of  $|F(hkl)|$ . Refinement using 1568 values of  $|F(hkl)| > 3\sigma$  was carried out with the SHELX76 program, incorporating neutral atomic scattering factors and anomalous scattering factors taken from the *International Tables for X-ray Crystallography* (1974).

The initial atomic coordinates were taken from the published  $\text{Er}_2\text{Ge}_2\text{O}_7$  structure (Smolin 1970). Refinement parameters included isotropic extinction and the  $g$ -term in the weighting scheme used in SHELX76. The temperature factors were refined aniso-

**Table 1.** Fractional coordinates and thermal parameters with ESDs in parentheses.  $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots)]$ , where the  $U_{ij}$  are in  $\text{\AA}^2$ .

Site	Point symmetry	$x$	$y$	$z$		
Tm	8(b)	1	0.875 78(3)	0.353 27(4)	0.135 61(2)	
Ge	8(b)	1	0.9004(1)	0.1523(1)	0.618 98(4)	
O1	4(a)	. . 2	0.8043(7)	0.1957(7)	0.7500(4)	
O2	8(b)	1	1.0794(6)	-0.0323(6)	0.6229(4)	
O3	8(b)	1	1.0625(6)	0.3380(6)	0.5709(3)	
O4	8(b)	1	0.6834(6)	0.1439(8)	0.5444(3)	
<hr/>						
	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Tm	0.0047(1)	0.0040(1)	0.0047(1)	0.0000(1)	-0.0004(1)	0.0002(1)
Ge	0.0039(2)	0.0044(2)	0.0057(2)	0.0003(2)	0.0003(2)	0.0001(2)
O1	0.013(1)	0.013(1)	0.007(2)	0.004(1)	0.004(1)	0.004(2)
O2	0.006(1)	0.005(1)	0.014(1)	-0.001(1)	-0.001(1)	-0.001(1)
O2	0.009(1)	0.006(1)	0.007(1)	0.000(1)	0.000(1)	-0.002(1)
O4	0.006(1)	0.016(2)	0.006(1)	-0.002(1)	-0.001(1)	-0.002(1)

tropically. In the final stages of refinement the 004 reflection was omitted, as its observed structure factor was found to be about twice the calculated value (because the pyrogermanates are very hard, having a (001) cleavage plane, this may be caused by multiple-scattering effects). The Fourier difference maps showed electron density between  $+5.0$  and  $-4.6 \text{ e \AA}^{-3}$ , the highest maxima being found in the vicinity of the Tm atom (within  $0.60$  to  $0.74 \text{ \AA}$ ). This extra electron density may result partly from the rather imprecise scattering factor for Tm in the *Tables* (refinement with the standard  $Tm^{3+}$  scattering factor only made matters worse) or from multiple scattering or anisotropic extinction. For space group  $P4_12_12$  the final agreement factors were  $R = 0.0276$ ,  $wR = 0.0369$ ; goodness-of-fit parameter  $S = 1.31$  with weights given by  $w = 1.3655/(\sigma^2 + 0.0000572F_0^2)$ ; average  $\Delta/\sigma < 0.01$  (maximum  $\Delta/\sigma < 0.05$ ). The isotropic extinction parameter (SHELX76) converged to  $0.0018(1)$ . Refinement with the sign of  $f''$  changed (equivalent to  $P4_32_12$  with atomic coordinates inverted) gave  $R = 0.0327$ ,  $wR = 0.0430$  and goodness of fit  $S = 1.31$ . Recalculation of the structure factors for models  $P4_12_12$  ( $\overline{xyz}$ ) and  $P4_32_12$  ( $xyz$ ) gave  $R \approx 0.30$  and  $wR \approx 0.48$ . 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 in table 2.

Figure 1(a) shows a  $Ge_2O_7$  unit in which the average Ge–O distance is  $1.748 \text{ \AA}$  (compared with  $1.749 \text{ \AA}$  in  $Er_2Ge_2O_7$ ,  $1.754 \text{ \AA}$  in  $Tb_2Ge_2O_7$  and  $1.77 \text{ \AA}$  in  $Eu_2Ge_2O_7$ ). This consists of two tetrahedra bridged by O1 to form an angle of  $135.5^\circ$ . Note that the Ge–O3 bond length is significantly longer than the other Ge–O lengths. The oxygen thermal ellipsoids are consistent with rigid-body motion of the tetrahedra hinged about O1 and with the centre of mass of the  $Ge_2O_7$  unit somewhere between the tetrahedra. Figure 1(b) shows the environment of  $Tm^{3+}$ . The most noticeable feature is that only seven oxygens are coordinated to Tm in the form of a distorted pentagonal bipyramid. As far as we know, no other  $Tm^{3+}$ -containing structure has hitherto been reported with sevenfold coordination. The average Tm–O distance is  $2.314 \text{ \AA}$  (compared with  $2.323 \text{ \AA}$  for Er–O in  $Er_2Ge_2O_7$ ,  $2.360 \text{ \AA}$  for Tb–O in  $Tb_2Ge_2O_7$  and  $2.38 \text{ \AA}$  for Eu–O in  $Eu_2Ge_2O_7$ ).

**Table 2.** Important interatomic distances and angles (a) Bond lengths (Å) and angles (deg). (b) Non-bonding distances (Å) between oxygens less than 3.3 Å and between heavy atoms less than 3.8 Å apart.

(a)			
Ge <sub>2</sub> O <sub>7</sub> <sup>†</sup>			
Ge–O1	1.751(3)	O1–Ge–O2	110.5(2)
Ge–O2	1.740(4)	O1–Ge–O3	114.6(1)
Ge–O3	1.769(4)	O1–Ge–O4	100.2(2)
Ge–O4	<u>1.732(4)</u>	O2–Ge–O3	95.0(2)
Mean	1.748	O2–Ge–O4	125.5(2)
		O3–Ge–O4	<u>111.8(2)</u>
		Mean	109.6
		Ge–O1–Ge <sup>‡</sup>	135.5(4)
TmO <sub>7</sub>			
Tm–O2 <sup>ii</sup>	2.197(3)	O2 <sup>ii</sup> –Tm–O2 <sup>iii</sup>	128.7(2)
Tm–O2 <sup>iii</sup>	2.345(3)	O2 <sup>ii</sup> –Tm–O3 <sup>iv</sup>	149.0(2)
Tm–O3 <sup>v</sup>	2.273(3)	O2 <sup>ii</sup> –Tm–O3 <sup>v</sup>	108.8(2)
Tm–O3 <sup>v</sup>	2.362(3)	O2 <sup>ii</sup> –Tm–O3 <sup>iii</sup>	68.1(1)
Tm–O3 <sup>iii</sup>	2.540(3)	O2 <sup>ii</sup> –Tm–O4 <sup>vi</sup>	84.7(1)
Tm–O4 <sup>vi</sup>	2.252(3)	O2 <sup>ii</sup> –Tm–O4 <sup>vii</sup>	80.1(1)
Tm–O4 <sup>vii</sup>	<u>2.231(3)</u>	O2 <sup>iii</sup> –Tm–O3 <sup>iv</sup>	70.6(1)
Mean	2.314	O2 <sup>iii</sup> –Tm–O3 <sup>v</sup>	80.0(1)
		O2 <sup>iii</sup> –Tm–O3 <sup>iii</sup>	63.8(1)
		O2 <sup>iii</sup> –Tm–O4 <sup>vi</sup>	143.4(2)
		O2 <sup>iii</sup> –Tm–O4 <sup>viii</sup>	87.8(1)
		O3 <sup>iv</sup> –Tm–O3 <sup>v</sup>	97.8(1)
		O3 <sup>iv</sup> –Tm–O3 <sup>iii</sup>	134.0(2)
		O3 <sup>iv</sup> –Tm–O4 <sup>vi</sup>	87.5(1)
		O3 <sup>iv</sup> –Tm–O4 <sup>vii</sup>	76.5(1)
		O3 <sup>v</sup> –Tm–O3 <sup>iii</sup>	80.2(1)
		O3 <sup>v</sup> –Tm–O4 <sup>vi</sup>	74.3(1)
		O3 <sup>v</sup> –Tm–O4 <sup>v</sup>	167.1(2)
		O3 <sup>iii</sup> –Tm–O4 <sup>vi</sup>	134.0(2)
		O3 <sup>iii</sup> –Tm–O4 <sup>vii</sup>	96.9(1)
		O4 <sup>vi</sup> –Tm–O4 <sup>vii</sup>	115.8(2)
(b)			
O1–O2	2.878(7)	Tm–Tm <sup>vii</sup>	3.565(1)
O1–O3	2.971(4)	Tm–Tm <sup>v</sup>	3.581(1)
O1–O4	2.679(4)	Tm–Tm <sup>ix</sup>	3.795(1)
O2–O3	2.588(6)		
O2–O4	3.087(6)	Ge–Ge <sup>‡</sup>	3.260(1)
O3–O4	2.899(6)	Ge–Ge <sup>x</sup>	3.790(1)
O2–O2 <sup>i</sup>	3.157(6)		
O2–O2 <sup>x</sup>	3.205(6)	Tm–Ge <sup>iii</sup>	3.216(1)
O2–O4 <sup>viii</sup>	3.174(6)	Tm–Ge <sup>vi</sup>	3.549(1)
O3 <sup>iv</sup> –O4 <sup>vi</sup>	3.129(6)	Tm–Ge <sup>vii</sup>	3.574(1)
O4 <sup>vi</sup> –O2 <sup>ii</sup>	2.998(6)	Tm–Ge <sup>v</sup>	3.646(1)
O3 <sup>v</sup> –O3 <sup>iii</sup>	3.160(6)	Tm–Ge <sup>iv</sup>	3.676(1)
O3 <sup>v</sup> –O2 <sup>iii</sup>	3.024(6)	Tm–Ge <sup>ii</sup>	3.746(1)
O3 <sup>v</sup> –O4 <sup>vi</sup>	2.788(6)		
O4 <sup>vii</sup> –O2 <sup>ii</sup>	2.849(6)		
O4 <sup>vii</sup> –O2 <sup>iii</sup>	3.174(6)		
O4 <sup>vii</sup> –O3 <sup>iv</sup>	2.788(6)		
O1–O4 <sup>xi</sup>	3.082(6)	O3–O2 <sup>xiv</sup>	2.667(6)

Table 2. (continued)

Symmetry codes:

(i) $-y + 1, -x + 1, -z + \frac{3}{2}$	(viii) $-y + \frac{3}{2}, x - \frac{1}{2}, z + \frac{1}{4}$
(ii) $-x + 2, -y, z - \frac{1}{2}$	(ix) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{4}$
(iii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{3}{4}$	(x) $y + 1, x - 1, -z + 1$
(iv) $-x + 2, -y + 1, z - \frac{1}{2}$	(xi) $-y + \frac{1}{2}, x - \frac{1}{2}, z + \frac{1}{4}$
(v) $y + \frac{1}{2}, -x + \frac{3}{2}, z - \frac{1}{4}$	(xii) $y, x, -z + 1$
(vi) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{3}{4}$	(xiii) $-y, -x + 2, -z + \frac{3}{2}$
(vii) $-y + 1, -x + 1, -z + \frac{1}{2}$	(xiv) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{4}$

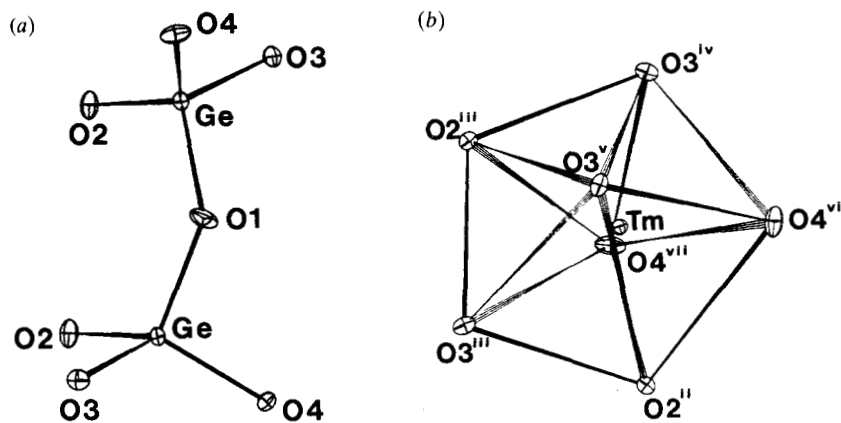
† Twofold axes passing through O1 atoms:  $xx0; xx\frac{1}{2}; x\bar{x}\frac{1}{4}; x\bar{x}\frac{3}{4}$ .

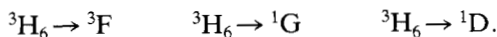
Figure 1. (a) The pyrogermanate group viewed on  $(010)$ . Thermal ellipsoids are plotted at the 75% probability level. The two tetrahedra are related by a diagonal twofold axis through O1. (b) The coordination polyhedron around  $Tm^{3+}$  at fractional position 0.876, 0.353, 0.136. Superscripts refer to symmetry codes in table 2.

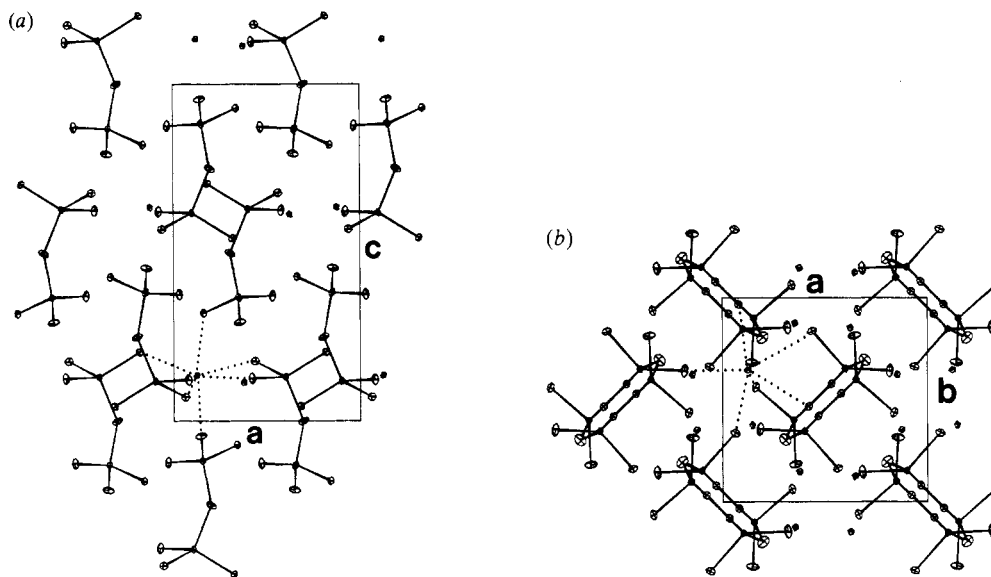
Figures 2(a) and (b) show projections on  $(010)$  and  $(001)$ , respectively. The  $Ge_2O_7$  groups lie on diagonal two-fold axes and form distinct units with their long axes along  $[001]$ . Each  $Tm^{3+}$  ion is surrounded by three other  $Tm^{3+}$  ions at distances between 3.565 and 3.581 Å, all outside the oxygen coordination sphere. Each  $TmO_7$  polyhedron shares three of its O–O edges with neighbouring polyhedra.

Figure 3 is a plot of the arrangement of  $GeO_4$  tetrahedra in the structure. It can be seen that there are columns along  $[001]$  consisting of four tetrahedra (two  $Ge_2O_7$  groups) in a  $c$ -repeat surrounded by eight  $Tm^{3+}$  ions.

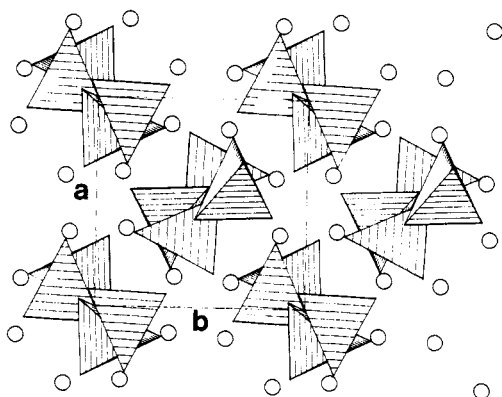
#### 4. Optical activity

Figure 4 shows the measured ORD for  $Tm_2Ge_2O_7$ . The otherwise smooth dispersion is slightly perturbed by three absorption bands of  $Tm^{3+}$  (Dieke 1968) corresponding to the transitions





**Figure 2.** Projections of the  $\text{Tm}_2\text{Ge}_2\text{O}_7$  structure showing thermal ellipsoids at the 75% probability level. Full lines are the Ge–O bonds. Dots indicate Tm–O contacts in  $\text{TmO}_4$  polyhedra. (a) (010) projection; (b) (001) projection.

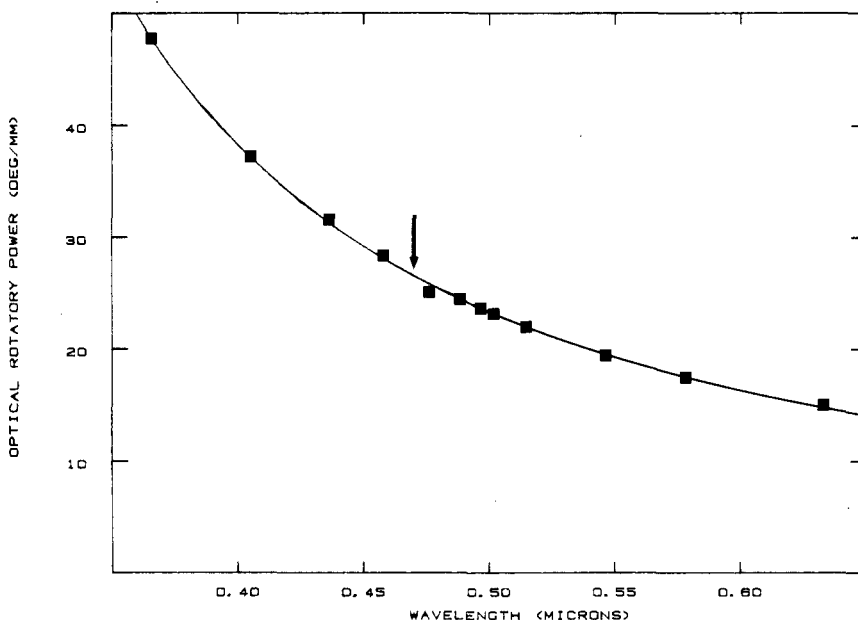


**Figure 3.** An (001) projection showing packing of tetrahedra. Circles are  $\text{Tm}^{3+}$  ions.

These occur at 0.65, 0.47 and 0.36  $\mu\text{m}$ , respectively. As far as we can tell, the bands at 0.65 and 0.36  $\mu\text{m}$ , which occur well away from the centre of our measuring range, do not influence the overall shape of the ORD curve (and certainly do not cause a change in sign). The band at 0.47  $\mu\text{m}$  only has a small (Cotton) effect on the ORD. This allows us to fit the curve overall with the Drude-type formula

$$\rho = \frac{-4.4336}{\lambda^2 - \lambda_0^2} - 2.6121$$

where  $\lambda$  is in  $\mu\text{m}$ ,  $\rho$  is in  $\text{deg mm}^{-1}$  and  $\lambda_0 = 0.1888 \mu\text{m}$ .



**Figure 4.** Modulus of the optical rotatory dispersion (ORD) of  $Tm_2Ge_2O_7$ . The arrow indicates the position of the circular dichroic transition at  $0.47 \mu m$  corresponding to the  $^3H_6 \rightarrow ^1G$  transition of  $Tm^{3+}$ . The full curve was obtained by fitting to the Drude-type formula in the text.

From the above, we see that the  $P4_12_12$  space group correlates with laevorotation of polarised light through the crystal. In order to understand this correlation, we have calculated the optical rotatory power (table 3) using the program of Devarajan and Glazer (1986). The problem here is complicated by the fact that there are four independent oxygens (the most polarisable atoms in the structure) plus significant contributions from  $Tm^{3+}$  and also from any lone-pair electrons of  $Tm^{3+}$ . Because of the uncertainties arising from having so many free parameters, our calculation was rather limited. By adjusting the polarisabilities of each type of oxygen, we found that, provided that the polarisability for O3 is made to be the largest and that for O4 smallest, we always obtain the correct sign for  $\rho$ . By careful adjustment we can get close to the correct value for  $\rho$ , but the calculated birefringence is larger than that observed experimentally (although the sign is correct). For instance, starting with isotropic polarisability volumes:

$$\begin{aligned} \alpha(O3) &= 2.57 \text{ \AA}^3 & \alpha(O1) = \alpha(O2) &= 2.14 \text{ \AA}^3 & \alpha(O4) &= 1.29 \text{ \AA}^3 \\ \alpha(Tm) &= 0.56 \text{ \AA}^3 & \alpha(Ge) &= 0.14 \text{ \AA}^3 \end{aligned}$$

we obtain, for  $\lambda = 0.6328 \mu m$ :

$$\rho = -15.1^\circ \text{ mm}^{-1} \quad n_o = 1.980 \quad n_e = 1.887 \quad \Delta n = -0.093$$

to be compared with the experimental values:

$$\rho = -15.0^\circ \text{ mm}^{-1} \quad n_o = 1.900 \quad n_e = 1.890 \quad \Delta n = -0.010.$$

It is possible to improve the birefringence calculation without seriously affecting the calculated value of  $\rho$  by starting with anisotropic polarisability volumes in which  $\alpha_{33} =$



**Table 3.** Results of calculations of refractive indices and optical rotatory power along [001] at  $\lambda = 0.6328 \mu\text{m}$  in  $\text{Tm}_2\text{Ge}_2\text{O}_7$ . The calculations were made using the program of Devarajan and Glazer (1986).

Polarisability volumes, $\alpha_{ij}$ ( $\text{\AA}^3$ ) †										
Tm	Ge	O1	O2	O3	O4	Conditions	$n_o$	$n_e$	$\Delta n$	$\rho$ (deg mm <sup>-1</sup> )
		2.46	2.46	1.97	1.97	O1 = O2 > O3 = O4	1.884	1.901	0.017	12.7
		2.18	2.18	2.18	2.18	O1 = O2 = O3 = O4	1.891	1.885	-0.005	-0.7
		1.77	1.77	2.48	2.48	O1 = O2 < O3 = O4	1.904	1.869	-0.035	-21.4
0.52	0.13	1.40	1.40	2.24	2.79	O1 = O2 < O3 < O4	1.956	1.935	-0.021	6.3
0.56	0.14	2.14	2.14	2.57	1.29	O3 > O1 = O2 > O4	1.980	1.887	-0.093	-15.1
0.56	0.14	1.31	1.97	3.15	1.31	O3 > O2 > O1 = O4	2.031	1.873	-0.158	-37.0
0.53	0.14	2.03	2.03	2.44	1.22	O3 > O1 = O2 > O4	1.902	1.895	-0.007	-11.1
0.51	0.13	1.95	1.95	2.63	1.17	O3 > O1 = O2 > O4	1.903	1.883	-0.020	-14.4
0.45	0.12	1.95	1.95	2.62	1.28	O3 > O1 = O2 > O4	1.901	1.889	-0.012	-14.4
0.44	0.11	1.95	1.95	2.63	1.29	O3 > O1 = O2 > O4	1.900	1.889	-0.011	-14.6
Experimental values							1.900	1.890	-0.010	-15.0
Estimated errors							0.001	0.001		0.1

†  $\alpha_{22} = \alpha_{11}$ ,  $\alpha_{33} = p\alpha_{11}$ ,  $\alpha_{ij} (i \neq j) = 0$ .  $p = 1.00$  for isotropic and  $p \neq 1.00$  for anisotropic input data.

$p\alpha_{11} = p\alpha_{22}$  for all atoms, with the ratio  $p \approx 1.06$ , e.g.

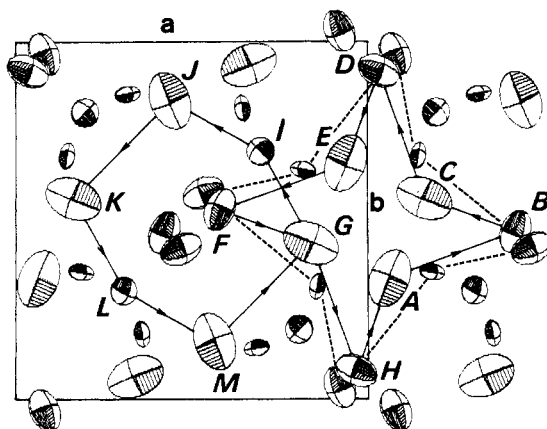
$$\begin{array}{ll} \alpha_{11}(\text{Tm}) = 0.44 \text{ \AA}^3 & \alpha_{33}(\text{Tm}) = 0.47 \text{ \AA}^3 \\ \alpha_{11}(\text{Ge}) = 0.11 \text{ \AA}^3 & \alpha_{33}(\text{Ge}) = 0.12 \text{ \AA}^3 \\ \alpha_{11}(\text{O3}) = 2.63 \text{ \AA}^3 & \alpha_{33}(\text{O3}) = 2.79 \text{ \AA}^3 \\ \alpha_{11}(\text{O1}) = \alpha_{11}(\text{O2}) = 1.95 \text{ \AA}^3 & \alpha_{33}(\text{O1}) = \alpha_{33}(\text{O2}) = 2.07 \text{ \AA}^3 \\ \alpha_{11}(\text{O4}) = 1.29 \text{ \AA}^3 & \alpha_{33}(\text{O4}) = 1.37 \text{ \AA}^3. \end{array}$$

This gives the result:

$$\rho = -14.6^\circ \text{ mm}^{-1} \quad n_\omega = 1.900 \quad n_\epsilon = 1.889 \quad \Delta n = -0.011.$$

It can be seen, therefore, that we can fit the optical quantities very closely by making suitable adjustments to the polarisabilities, despite the fact that near the chosen wavelength there may be a weak Cotton effect at  $0.47 \mu\text{m}$ . Using these final polarisability volumes, we also calculate the rotation about the  $[100]$  ( $= [010]$ ) direction to be  $+3.6^\circ \text{ mm}^{-1}$ . This change in sign is consistent with the prediction of Pine and Dresselhaus (1972). However, because this direction is also birefringent this value cannot easily be measured and so confirmation of this prediction must wait until this can be done.

It is interesting to identify those structural features that may be responsible for the optical rotation. We have consistently found in our calculations (table 3) that it is O3 that has the major role in determining the optical rotation. Probably this is because the Ge–O3 distance is the largest among the Ge–O lengths, and so the electron cloud around O3 is likely to be more easily polarised by the electric field from the neighbouring atoms. In addition, as described by Glazer and Stadnicka (1986), we look for helical arrangements of the most polarisable atoms, here the oxygens. In figure 5, which shows the calculated polarisability ellipsoids, we mark two structural helices: ABCDEFGH which is denoted RS2/8 (according to the definition given by Glazer and Stadnicka) and



**Figure 5.** Oxygen polarisability ellipsoids on (001) as calculated using the Devarajan and Glazer program. The RS2/8 and RS2/6 helices are marked by arrows. ABCDEFGH and IJKLMG refer to RS2/8 and RS2/6 structural helices, respectively. The atom fractional heights are: for RS2/8, A, 0.07, B, 0.13, C, 0.32, D, 0.38, E, 0.57, F, 0.63, G, 0.82 and H, 0.88; for RS2/6, I, 0.00, J, 0.18, K, 0.32, L, 0.50, M, 0.68 and G, 0.82. RS2/8 tends to rotate light to the left and RS2/6 to the right.

is formed by alternating O3 and O2 (distances of 2.667 and 3.024 Å); IJKLMG denoted RS2/6 and formed by alternating O3 and O1 (distances of 2.971 and 3.160 Å). In the RS2/8 helix, the thermal ellipsoids (figure 2), at least for O3, are directed somewhat radially with respect to the helix axis and, as shown by Glazer and Stadnicka, should be most polarisable tangentially to the helix. This can be seen to be the case in figure 5. We therefore expect the light to rotate in the same sense as the RS2/8 helix, i.e. in a laevorotatory fashion. In the RS2/6 helix, the thermal ellipsoids are tangential, and hence the polarisability ellipsoids are radial, again as borne out by the calculation (figure 5), and so we expect this helix to contribute towards rotating the light in the opposite sense. Thus the two helices act in opposition to one another. However, the O–O distances in the RS2/8 helix are significantly shorter on average than those in the RS2/6 helix, and so it is the RS2/8 helix that dominates.

Moreover, there is another RS2/8 helix made from alternating O2 and O4 (distances of 2.849 and 2.998 Å), marked by broken lines in figure 5. This also will contribute towards laevorotation, but to a smaller extent, because the O4 polarisability is significantly smaller.

In our analysis, we have ignored the possibility that lone-pair electrons on the Tm<sup>3+</sup> ion should be taken into account, as was done by Thomas (1988) for TeO<sub>2</sub>. Although extra electron density was found near the Tm atom, because of the high absorption and extinction in this crystal we are unable to identify this density categorically as being due to the lone pairs, nor is there much information about lone-pair distributions for Tm<sup>3+</sup> available in the literature.

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