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## The crystal structure and optical activity of potassium dithionate, $K_2S_2O_6$

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**Abstract.** The absolute chirality of potassium dithionate,  $K_2S_2O_6$ ,  $M_r = 238.3$ , trigonal, space group  $P321$ ,  $a = 9.782(1) \text{ \AA}$ ,  $c = 6.298(2) \text{ \AA}$ ,  $V = 521.9(1) \text{ \AA}^3$ ,  $Z = 3$ ,  $R = 0.024$ ,  $wR = 0.031$  for 2586 unique observed reflections, has been determined at room temperature through a combination of single-crystal x-ray diffraction, including anomalous scattering, and optical study. Using a classical point dipole–dipole theory, good agreement has been obtained between the calculated and observed optical activity and refractive indices at room temperature ( $\rho = -6.57^\circ \text{ mm}^{-1}$  along  $[001]$ ,  $n_e = 1.512$ ,  $n_o = 1.453$  at a wavelength of 632.8 nm). The polarizabilities of the different atoms have also been determined by means of this theory. It has been found that in order to fit the optical data, it is necessary that the oxygen atoms must show quite large anisotropic polarizabilities. The structural features responsible for the optical rotation have been identified. In this way, a visual correlation between the sign of the optical activity and the arrangement of atoms in the crystal structure has been established.

### 1. Introduction

The first crystallographic investigation of potassium dithionate (hereafter referred to as KSO), at room temperature, was performed by Barnes and Helwig (1931) and by Huggins and Frank (1931) who assigned it to the space group  $P321$ . The structure of KSO was later modified by Helwig (1932) and by Huggins (1933). These two assignments differ only in the orientations of the oxygen atoms about the S–S bonds. A study of the nature of twinning in potassium and rubidium dithionate was carried out by Barnes and Wendling (1938), who suggested that accurate optical activity (hereafter OA) measurements should be carried out to decide between the different possibilities of twin formation. A more recent structure determination of KSO was undertaken by Stanley (1956) who arrived at an  $R$ -factor of 0.08 and 0.07 for the  $hk0$  and  $h0l$  reflections, respectively. This structural result is close to that previously obtained by Huggins and Frank.

KSO shows a substantial OA ( $16^\circ \text{ mm}^{-1}$ ) at a wavelength of 435 nm for light propagating along the optic axis. The material is positive uniaxial and quite highly birefringent ( $n_e - n_o = +0.06$  at 435 nm). The OA in KSO at room temperature and in the spectral range 240–800 nm was measured by Belyaev and Perekalina (1967). The temperature variation of the OA from 298 K at 435 nm is also reported in this work. The

OA was found to decrease with temperature in contrast to the behaviour displayed by other crystals such as quartz. As the structure has no screw axis, those authors attributed the origin of the OA to the  $S_2O_6^{2-}$  ions, regarding them as linked by a pseudotrigonal  $3_1$  axis. The potassium atom contribution was found to be negligible.

Other optical properties of KSO have also been studied. For example, an electro-optic coefficient  $r_{11} = 0.263 \text{ pm V}^{-1}$  was measured by Silker (1964). Second-harmonic generation has also been studied in KSO crystals, and it has been verified that the material presents phase-matching possibilities due to its high birefringence and low dispersion (Hobden *et al* 1966).

In this work the structure of KSO is redetermined at room temperature and more accurate atomic parameters and bond lengths are obtained. Moreover, measurements of the OA along the optic axis and of the refractive indices are presented. From the structural and optical data, the absolute chirality is established and the helicoidal structural atomic arrangements in the crystal responsible for the appearance of OA are identified.

## 2. Structural results

Crystals of KSO were prepared by adding potassium hydroxide to an aqueous solution of  $MnS_2O_6$ . Transparent crystals of very good optical quality were obtained by slow evaporation at room temperature.

A good optical quality crystal was cut and polished on a (001) section after a small piece was removed for structure measurements. The section, when viewed in conoscopic illumination between crossed polars, gave a good uniaxial figure which showed no variation with the position of the slice. There was no evidence of twinning. On insertion of a quarter wave plate above the crystal an Airy spiral was obtained, which demonstrated that the crystal was optically laevorotatory. The existence of OA, and the symmetry of precession photographs at room temperature of the layers  $l = 0, 1$  and  $2$ , confirmed the trigonal symmetry  $32$  and clearly excluded the presence of twinning in the crystal used for structure and optical measurements.

The small piece removed from the laevorotatory sample was ground to a sphere and used for the measurements of the diffraction intensities. Details of the crystal data and the data collection are presented in table 1. The overall diffraction symmetry of the measured intensities was  $32$ , thus corroborating the previous choice of space group  $P321$ . All the calculations and refinement were performed with the X-RAY program (Stewart *et al* 1972). Using as starting coordinates those of Stanley (1956), the refinement was straightforward. Final atomic coordinates and thermal parameters are listed in table 2.

A projection of the structure on (001) is shown in figure 1 with atomic thermal ellipsoids for all atoms. The interatomic distances and angles in the  $S_2O_6^{2-}$  ions are in agreement with the values reported before and are listed in table 3. Each sulphur is tetrahedrally surrounded by another sulphur and three oxygens. Each potassium is bonded to six oxygen atoms and each oxygen is associated with two potassium ions. The corresponding interatomic distances and angles are listed in table 4. Table 5 shows the anisotropic thermal parameters for all the atoms. As can be seen, the  $U_{22}$  component of the thermal parameters of one atom (O3) has an anomalous large value. Since no superstructure reflections were observed on the diffraction pattern, the existence of a superstructure should be discarded. We have then to assume the presence of some disorder for this atom, this also explaining the short value of the O3-S3 distance in comparison with those of O1-S1 and O2-S2 (see table 3).

**Table 1.** A summary of experimental conditions and refinement details.

Crystal colour, shape and size	Colourless, sphere ( $r = 0.187$ mm)
Diffractometer	Enraf–Nonius CAD-4
Radiation	Mo $K\alpha$ ( $0.7107 \text{ \AA}$ )
No of reflections and angular range for lattice parameters	25 $11^\circ < \theta < 17^\circ$
Scan mode	$\theta-2\theta$
Range of $h, k, l$	$\pm 17, \pm 17, \pm 11$
$(\sin \theta/\lambda)_{\max}$	$0.9033 \text{ \AA}^{-1}$
Intensity control	3 monitored every 7200 s, no significant variation
Orientation control	3 monitored every 300 reflections
No of reflections measured	13 398
No of unique reflections	2669
No of unique observed reflections	2494 ( $I_{\text{obs}} > 3.0\sigma(I_{\text{obs}})$ )
$R_{\text{int}}$ on intensities	0.048
$f, f'$ and $f''$ for neutral atoms	<i>International Tables for X-ray Crystallography</i>
Corrections applied	Polarization, Lorentz and absorption
No of reflections in the refinements	2586
Weights	$w = 1/\sigma^2(F_{\text{obs}})$
Number of parameters refined	49
$R$	0.024
$wR$	0.031
Goodness of fit ( $S$ )	1.124
Maximum and average shift/e.s.d.	0.0105 and 0.0015
$(\Delta\rho)_{\max}$ in the $\Delta F$ synthesis	$0.7 \text{ e \AA}^{-3}$
Extinction, mosaic distribution	0.35(3)
Absolute structure parameter	0.03(4) (Flack 1983)

**Table 2.** Atomic coordinates and equivalent thermal parameters in laevorotatory  $K_2S_2O_6$  (e.s.d. are given in parenthesis).

Atom	$x$	$y$	$z$	$U$ (eq.)
K1	0.619 48(3)	0	0	0.23 75(4)
K2	0.293 63(3)	0	0.5	0.030 52(5)
S1	0	0	0.829 10(5)	0.021 70(4)
S2	0.333 33	0.666 67	0.737 90(5)	0.020 06(4)
S3	0.333 33	0.666 67	0.398 59(5)	0.022 43(4)
O1	0.155 7(1)	0.124 1(1)	0.768 2(2)	0.035 2(2)
O2	0.204 6(1)	0.511 7(1)	0.798 5(1)	0.027 3(2)
O3	0.175 0(1)	0.623 5(2)	0.344 1(2)	0.059 0(5)

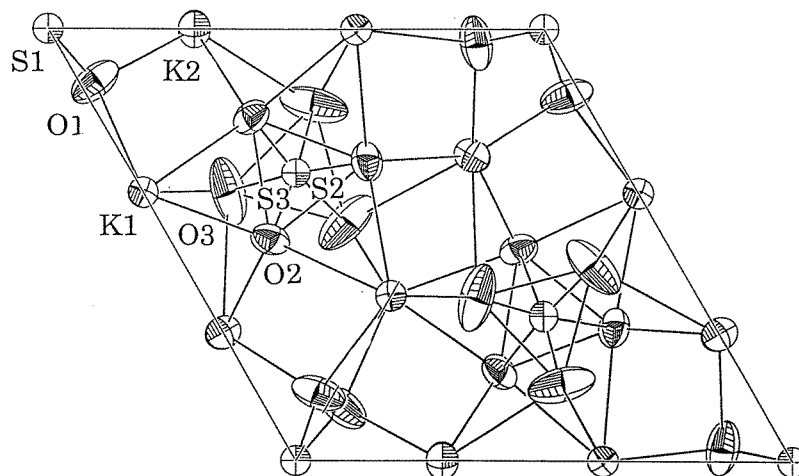
**Table 3.** Interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) within the dithionate ions.

S1–S1 <sup>a</sup>	2.1527(8)	S1 <sup>a</sup> –S1–O1 <sup>b</sup>	105.38(4)
S2–S3	2.1370(8)	S3–S2–O2	105.20(4)
S1–O1 <sup>b</sup>	1.4463(9)	S2–S3–O3	103.91(5)
S2–O2	1.4563(7)		
S3–O3	1.428(1)		

<sup>a</sup>  $y, x, -z$ .<sup>b</sup>  $x - 1, y - 1, z$ .

### 3. Optical properties and calculations

The OA along the optic axis was measured as a function of temperature (from room temperature to 313 K) using a High-Accuracy Universal Polarimeter (Kobayashi and



**Figure 1.** An ORTEP (Johnson 1965) plot of the  $K_2S_2O_6$  structure viewed along [001]. This structure corresponds to a laevorotatory crystal. Displacement ellipsoids are drawn at the 50% probability level for all atoms.

**Table 4.**  $K^+$  ion contact distances ( $\text{\AA}$ ).

$K(1)-O(1)^a$	2.783(1)	$K(2)-O(1)^b$	2.790(1)
$K(1)-O(1)^c$	2.783(1)	$K(2)-O(1)^d$	2.790(1)
$K1-O2^a$	2.9028(9)	$K2-O2^c$	2.797(1)
$K1-O2^e$	2.9729(9)	$K2-O2^f$	2.7967(9)
$K1-O2^g$	2.972(1)	$K2-O3^e$	2.964(2)
$K1-O2^c$	2.9028(9)	$K2-O3^f$	2.964(2)
$K1-O3^h$	2.750(1)		
$K1-O3^f$	2.750(1)		

<sup>a</sup>  $1 - y, x - y, z.$

<sup>b</sup>  $x, y - 1, z.$

<sup>c</sup>  $1 - x, y - x, -z.$

<sup>d</sup>  $x - y + 1, 1 - y, 1 - z.$

<sup>e</sup>  $1 + y - x, 1 - x, z.$

<sup>f</sup>  $y, x - 1, 1 - z.$

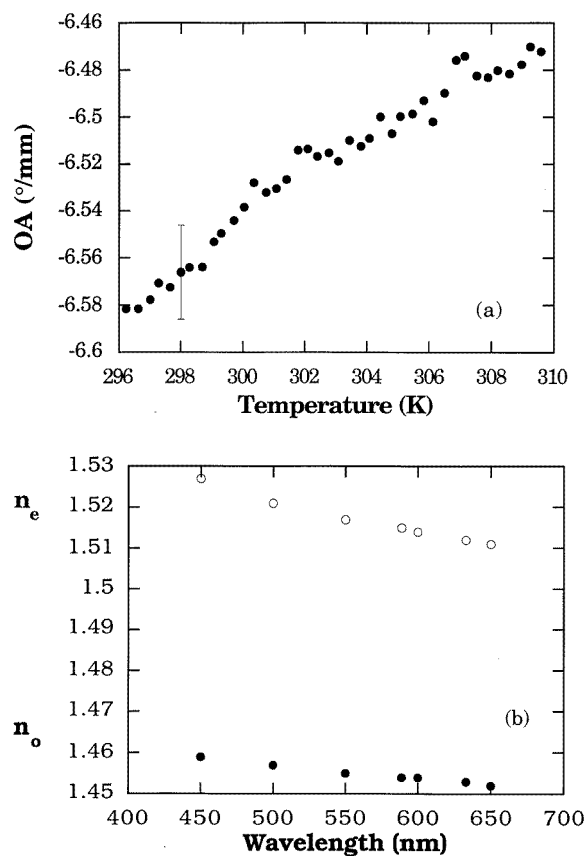
<sup>g</sup>  $y, x - 1, -z.$

<sup>h</sup>  $1 + y - x, 1 - x, z - 1.$

Uesu 1983). The wavelength was 632.8 nm. Refractive indices were measured at room temperature using an Abbe refractometer illuminated with a Xe arc lamp and a monochromator. The temperature dependence of the OA is shown in figure 2(a) and the variation of the refractive indices at room temperature as a function of the wavelength is shown in figure 2(b). As can be seen, the material presents normal dispersion in the visible range, and the OA shows a slight temperature dependence, decreasing somewhat as the temperature is raised. The optical results are consistent with those of Belyaev and Perekalina (1967) and Hobden *et al* (1966). The OA in a direction perpendicular to the optic axis could not be measured because of the high birefringence of the materia, which overwhelms the effects produced by the OA.

**Table 5.** Anisotropic thermal parameters ( $\text{\AA}^2 \times 100$ ) for  $K_2S_2O_6$  in space group  $P321$ , with e.s.d.s in parentheses.

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
K1	2.531(8)	2.284	2.309(9)	1.142(5)	0.025(4)	0.050
K2	2.756(9)	3.436	2.97(1)	1.718(8)	0.159(5)	0.318
S1	2.212	2.212	2.09(1)	1.106(4)	0.000	0.000
S2	1.967	1.967	2.08(1)	0.984(4)	0.000	0.000
S3	2.300	2.13(1)	2.13(1)	1.150(4)	0.000	0.000
O1	2.95(4)	4.56(5)	3.06(3)	0.13(3)	0.99(3)	-0.59(3)
O2	2.92(3)	2.33(3)	2.94(3)	0.73(3)	0.08(2)	0.66(2)
O3	3.20(5)	11.1(1)	3.35(4)	-0.45(3)	1.78(6)	

**Figure 2.** (a) Optical rotatory power along [001] of  $K_2S_2O_6$  as a function of temperature. (b) Variation of the refractive indices of  $K_2S_2O_6$  at room temperature as a function of wavelength.

The OA along [001] and the refractive indices were calculated, for a wavelength of 632.8 nm, using a computer program (OPTACT) based on the classical dipole-dipole theory by Devarajan and Glazer (1986).  $K_2S_2O_6$  can be considered an ionic crystal and, consequently, the dipolar approximation used in the calculation of the optical properties should work quite well. There are three distinct types of oxygen atom in the structure, which form the  $S_2O_6^{2-}$

ion (named O1, O2 and O3 in table 2), and two different potassium atoms (designated as K1 and K2 in table 2). These were the atoms considered in the OA and refractive index calculations. As for other dithionates, the contribution of the sulphur atoms to the optical properties was assumed to be negligible (de Matos Gomes *et al* 1994). The atomic coordinates used in the calculations are those given in table 2. The values to be fitted are  $n_0 = 1.453(1)$ ,  $n_e = 1.512(1)$  and  $\rho = -6.57(2)^\circ \text{ mm}^{-1}$  for  $\lambda = 632.8 \text{ nm}$ .

Two isotropic polarizabilities were initially considered, one for all the oxygen atoms ( $\alpha(\text{O})$ ) and the other for the potassium ions ( $\alpha(\text{K})$ ). A larger value was assigned to the oxygens, which is consistent with the values found by Tessman *et al* (1953) in fitting refractive index data for several compounds. The best fit was obtained with polarizability volumes  $\alpha(\text{K}) = 0.400 \text{ \AA}^3$  and  $\alpha(\text{O}) = 1.790 \text{ \AA}^3$ , yielding  $n_0 = 1.511$ ,  $n_e = 1.426$  and  $\rho = -7.2^\circ \text{ mm}^{-1}$ . It should be noted that the refractive indices are interchanged, that is, the birefringence has a sign opposite to that experimentally observed. With the aim of correcting the birefringence sign, calculations were also performed by considering two different oxygen atoms: the same polarizability was given to O1 and O2 and a smaller value was assigned to O3, based on the fact that these atoms have larger thermal parameters. Again the birefringence turned out to be negative. In fact, if isotropic polarizabilities are assigned to all atoms, it appears to be impossible to obtain a positive birefringence (some additional tests indicated that a positive birefringence can be obtained only if negative isotropic polarizabilities are assigned to the oxygens, which obviously does not have any physical meaning).

Therefore, in order to account for the observed optical properties, anisotropic polarizabilities had to be used as input parameters in the OPTACT program. In principle, one can assign anisotropic polarizabilities to both potassium and oxygen atoms. Moreover, since we have three different oxygens and two different potassiums, up to five different polarizability tensors could be introduced in the calculations. However, as only three quantities have to be fitted ( $n_0$ ,  $n_e$  and  $\rho$ ), it seems more reasonable to keep the number of unknown parameters limited to a maximum of three. In this situation, we decided to use the same polarizabilities for the atoms of a particular element and assign a (uniaxial) polarizability tensor to the oxygen atoms. This can be justified in terms of the different anisotropy and orientation of the thermal ellipsoids of potassium and oxygen. Since the anisotropic polarizabilities usually tend to be largest in directions where the thermal motion is smallest (Glazer and Stadnicka 1986), the parameters were chosen to be  $\alpha(\text{K})$ ,  $\alpha_{11}(\text{O}) = \alpha_{22}(\text{O})$  and  $\alpha_{33}(\text{O})$ . Here  $\alpha_{11}(\text{O})$ ,  $\alpha_{22}(\text{O})$  and  $\alpha_{33}(\text{O})$  are the diagonal elements of the polarizability tensor of oxygens. The results of the calculations are given in table 6. For comparison purposes, we have also included other selected results in which anisotropic polarizabilities were assigned only to the O3 atoms (in view of their large thermal motion) and to the O1 and O3 atoms. As can be seen, rather good fits were obtained in all cases. However, the most convincing solution seems to be the first, since it is not easy to understand on physical grounds the huge anisotropy displayed by some of the oxygens in the second and third fits. Hereafter, we will continue the discussion considering only the first solution.

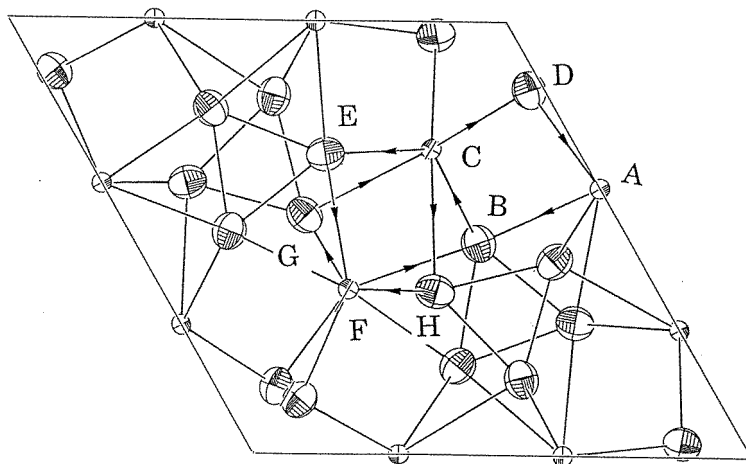
For the input polarizabilities  $\alpha_{11}(\text{O}) = \alpha_{22}(\text{O}) = 1.546 \text{ \AA}^3$ ,  $\alpha_{33}(\text{O}) = 2.063 \text{ \AA}^2$  and  $\alpha(\text{K}) = 0.655 \text{ \AA}^3$ , the values  $n_0 = 1.453$ ,  $n_e = 1.512$  and  $\rho = -6.0^\circ \text{ mm}^{-1}$  for  $\lambda = 632.8 \text{ nm}$  were obtained. Complementary calculations showed that small changes in  $\alpha_{11}(\text{O})$  only modify  $n_0$  while changes in  $\alpha_{33}(\text{O})$  only modify  $n_e$  with no important changes in the OA in either case. On the other hand, a small change in  $\alpha(\text{K})$  affects both the refractive indices and the OA. Obviously, large changes in the polarizabilities of the oxygen atoms also change the OA, as expected. It is interesting to point out that the use of anisotropic input polarizabilities for the oxygen atoms has already been found to be rather important

**Table 6.** Results of calculations of refractive indices and optical rotatory power along [001] at  $\lambda = 632.8$  nm. The calculations were made using the program OPTACT (Devarajan and Glazer 1986). Input polarizability values are given in cubic ångströms.

$\alpha(K)$	$\alpha_{11}(O1)$	$\alpha_{33}(O1)$	$\alpha_{11}(O2)$	$\alpha_{33}(O2)$	$\alpha_{11}(O3)$	$\alpha_{33}(O3)$	$n_e$	$n_o$	$\rho$ ( $^\circ$ mm $^{-1}$ )
0.400	1.790	1.790	1.790	1.790	1.790	1.790	1.426	1.511	-7.2
0.655	1.546	2.063	1.546	2.063	1.546	2.063	1.512	1.453	-6.0
0.655	1.546	1.546	1.546	1.546	1.546	3.330	1.514	1.452	-5.9
0.655	1.546	2.350	1.546	1.546	1.546	2.350	1.515	1.453	-6.1
		Experimental values					1.512	1.453	-6.75

for finding a precise agreement between calculated and observed optical properties of some compounds such as  $ZnSeO_4 \cdot 6H_2O$  (Stadnicka *et al* 1988) or  $(NH_4)_2H_2PO_4$  (Stadnicka *et al* 1992). In contrast to the present case, but with an obvious physical meaning, in these works we  $\alpha_{33} < \alpha_{11} = \alpha_{22}$  was made for the oxygen atoms, in order to obtain a negative birefringence.

The sense of rotation of the light can now be correlated visually with the structural arrangement of atoms. In order to achieve this objective, we followed the theory by Glazer and Stadnicka (1986) which links the structural and optical chiralities using a simple visual approach based on the concept of anisotropic polarizabilities. The anisotropy of the atomic polarizabilities on the plane perpendicular to the optic axis was supposed to be well described by the so-called effective polarizability tensors (Devarajan and Glazer 1986). These effective polarizabilities were obtained from the polarizability tensors obtained in the OPTACT calculations.



**Figure 3.** A view of laevorotatory  $K_2S_2O_6$  along [001] showing the effective polarizability ellipsoids for oxygen and potassium atoms. The ellipsoids correspond to a final calculated optical rotation of  $-6.0^\circ$  mm $^{-1}$  with input polarizability values  $\alpha_{11}(K) = \alpha_{22}(K) = 1.546 \text{ \AA}^3$ ,  $\alpha_{33}(K) = 2.063 \text{ \AA}^3$  and  $\alpha(K) = 0.655 \text{ \AA}^3$ . The arrows denote the helices of atoms identified as the structural origin of the observed optical rotation.

According to the rules given by Glazer and Stadnicka (1986), we found three crystallographically independent non-symmetric structural helices that may give rise to



optical rotation. These are shown in figure 3 together with the effective polarizability ellipsoids for oxygen and potassium atoms. The helices are the following: a left-handed helix formed by O1, O2, K1 and K2 atoms (marked ABCD), another left-handed helix formed by K1, K2 and O3 atoms (marked HFGC) and finally a right-handed helix formed by K1, K2 and O2 atoms (marked EFBC). On the ABCD and HFGC helices, the radial components of the polarizability ellipsoids are larger than the tangential ones and the plane of polarization of the incident light should rotate anticlockwise for light coming towards the observer. Similarly, on the EFBC helix, the radial components of the polarizability ellipsoids are larger than the tangential ones and the plane of polarization of the incident light should rotate clockwise for light coming towards the observer. However, the effect of the HFGC and EFBC helices is cancelled, as they have bond lengths of about the same magnitude and the atoms forming the helices have the same polarizability. Consequently, the origin of the OA can be attributed exclusively to the helix of atoms ABCD and the crystal should be laevorotatory.

Finally, we will mention that the effective polarizability ellipsoids of the oxygen and potassium atoms are roughly perpendicular to their corresponding thermal ellipsoids, as can be seen from comparison between figures 1 and 3, thus showing that the anisotropic polarizabilities tend to be largest in the neighbourhood of the surrounding atoms, i.e., along directions where the thermal ellipsoids are smallest. This prediction (Glazer and Stadnicka 1986) has been observed to happen for a large number of materials (see e.g. Devarajan and Glazer 1986, Stadnicka *et al* 1988, Ortega *et al* 1993, de Matos Gomes *et al* 1994) and seems, therefore, to be a rule of practically general application.

#### 4. Conclusions

The structural origin of the optical rotation and refractive indices of KSO has been investigated using a classical anisotropic polarizability theory. The arrangement of potassium and oxygen atoms in non-symmetric structural helices has been identified as the origin of the OA. Oxygen atoms (mainly O1 and O3) are thermally very anisotropic on a plane perpendicular to the *c*-axis and, consequently, present rather anisotropic polarizability tensors on a plane containing the optic axis. It is this anisotropy that makes the material display a positive birefringence. Finally, it has also been shown that the thermal and effective polarizability ellipsoids are perpendicular to each other in KSO, as has been found in other optically active crystals.

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