

Optical Rotatory Dispersion and Absolute Optical Chirality of Strontium and Calcium Dithionate Tetrahydrate, $\text{SrS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ and $\text{CaS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$

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Abstract

Using classical point dipole–dipole theory, excellent agreement is obtained between the calculated and observed optical rotatory dispersion (ORD) and refractive indices. A link between the ORD observed and the absolute configuration of $\text{SrS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ and $\text{CaS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ is made using the structural approach to ORD developed by Glazer & Stadnicka [*J. Appl. Cryst.* (1986), **19**, 108–122]. It is also shown that the thermal and anisotropic polarizability ellipsoids are perpendicular to one another for water O atoms.

1. Introduction

The optical rotatory dispersion (hereafter ORD) in $\text{SrS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ and $\text{CaS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ was discovered by Pape (1867) and measured for the first time in the visible range by Rose (1910). Belyaev & Perekalina (1967) extended the spectral range of the rotatory dispersion in the ultraviolet and approached the absorption band. The origin of the ORD observed was attributed to the $\text{S}_2\text{O}_6^{2-}$ ion by Klimova & Perekalina (1976), based on an oscillator model in which electronic transitions were responsible for the ORD and the role of the cation was regarded as an external ‘vicinal’ action.

Both of these materials show a small ORD in the visible range of the spectrum. The structure of $\text{SrS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ has been redetermined by de Matos Gomes (1991*a*) and it was shown that the structure is disordered with a twofold axis along [110], the disorder arising from the $\text{S}_2\text{O}_6^{2-}$ ion occupying two sites on either side of this axis. The space group $P6_422$ was assigned to a dextrorotatory crystal.

The structure of $\text{CaS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ has also been determined by de Matos Gomes (1991*b*). It was shown that $\text{CaS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ is a superstructure of $\text{SrS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ with doubling of all three axes, and its average structure is very similar to the structure of $\text{SrS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ with the $\text{S}_2\text{O}_6^{2-}$ ion occupying two sites on either side of a twofold axis along [110]. The crystal used for structural and optical measurements

was dextrorotatory and the space group $P6_422$ was assigned to the average structure.

2. Optical rotatory dispersion of $\text{SrS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ and $\text{CaS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$

2.1. Experimental

Crystals of $\text{SrS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ and $\text{CaS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ (hereafter SrDH and CaDH respectively) were cut and polished on (001) after a small piece had been removed for X-ray structural studies. The crystals were observed between crossed polars and a uniaxial figure could be seen in both of them. When a quarter-wave plate was inserted above the crystals, Airy’s spirals were obtained which demonstrated that the crystals were both optically dextrorotatory. The ORD dispersion curve for a wavelength range 350–700 nm was measured (Figs. 1*a* and 1*b*), using the High Accuracy Universal Polarimeter (Moxon & Renshaw, 1990) built in the Clarendon Laboratory, and agreed well with the measurements of Klimova & Perekalina (1976).

2.2. Optical rotatory dispersion

The SrDH structure is disordered at room temperature and is equivalent to the average structure of CaDH (de Matos Gomes, 1991*b*). A locally ordered form was considered for the purposes of the ORD calculations and its interpretation. As already mentioned, the two structures are very similar and the configuration used in the calculations corresponds to a structure in space group $P6_4$ (Figs. 2*a* and 2*b*). The atomic coordinates used in the optical calculations are listed in Table 1.

We could equally well have considered the other configuration (related by a twofold axis along [110]) since the same ORD and optical anisotropy is displayed by both of them.

A link between ORD and absolute configuration was now sought, using the guidelines of Glazer & Stadnicka (1986) (hereafter GS). According to them, the most polarizable atoms are the most important, here the metal (Sr or Ca) and O atoms. Using the computer program written by Devarajan & Glazer

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(1986) (hereafter DG), based on classical dipole-dipole polarizability theory, the optical rotatory dispersion and refractive indices were calculated with the structural data and isotropic polarizabilities supplied for the more important atoms. There are five independent O atoms in each structure, three of which (O1–O3) form the $S_2O_6^{2-}$ ion and the other two (O4 and O5) belong to the water molecules. As only three parameters are fitted in the calculations, three different types of atoms were considered: metal (Sr or Ca), O1–O3 named as O(S), and O4–O5 named O(W) in the optical calculations. For SrDH, the average S–O distance is 1.45 Å and the Sr–O(W) distance is 2.612 Å. Then, as the S–O bonds are stronger, larger polarizability volumes were assigned to the O(W) than to the O(S) atoms. For a wavelength of 492 nm and input polarizability volumes $\alpha_{Sr} = 1.593$, $\alpha_{O(S)} = 1.163$ and $\alpha_{O(W)} = 1.929 \text{ \AA}^3$ an excellent fit to the experimental results was obtained (Table 2).

For CaDH the S–O average bond length is 1.45 Å and the Ca–O(W) distance is 2.457 Å and so, as before, larger polarizability volumes were assigned to O(W) than to O(S). For a wavelength of 492 nm and input polarizability volumes $\alpha_{Ca} = 0.59$, $\alpha_{O(S)} = 1.195$ and $\alpha_{O(W)} = 1.977 \text{ \AA}^3$, again an excellent fit to the experimental results was obtained (Table 3).

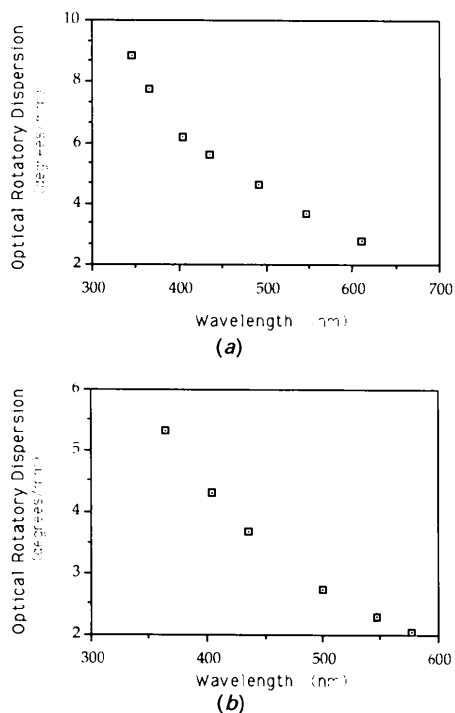


Fig. 1. Observed optical rotatory dispersion curves for (a) SrDH and (b) CaDH.

2.3. Discussion

For SrDH the more polarizable atoms are, as expected, the O(W) atoms followed by Sr while for CaDH the more polarizable atoms are the O(W) and O(S). This agrees with the polarizability values found by Tessman, Katta & Shockley (1953) in fitting refractive indices for several strontium and calcium compounds. Using the structural-helix theory (GS) together with the computer calculations, helices formed by the most polarizable atoms were looked for in the structure, with the aim of explaining the ORD. Two $RS_2/3$ (as defined by GS) helices, *ABCDEF* and *GHIJKL*, consisting of O(W) atoms (Figs. 3a and 3b) were found.

For SrDH (Fig. 3a), the polarizability ellipsoids of the O5 atoms (atoms *ACE* and *GIK*) are oriented radially towards the helix axis, while for the O4 atoms (atoms *BDF* and *HJL*), the radial component is much larger than the tangential one. GS showed that for radially directed polarizability the optical rotation should be *opposite* in sense to that of the helix, whereas when directed tangentially, the light should rotate in the *same* sense as the helix. Therefore, we must expect that it will give a dextrorotatory contribution to the ORD. In these helices the distances between O4–O5 are 2.785 and 4.793 Å, the

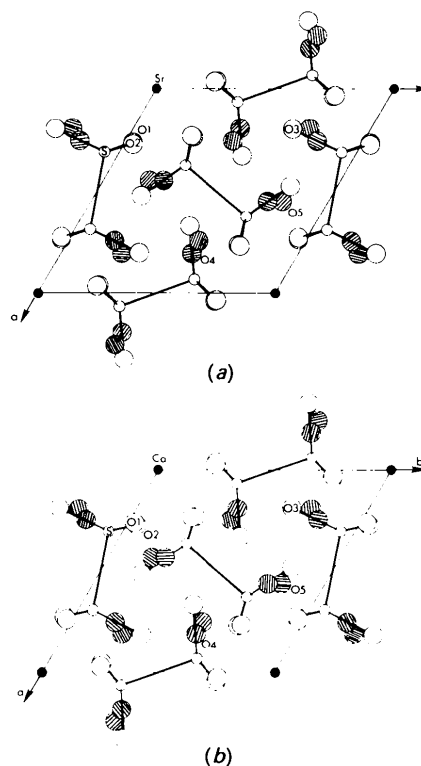


Fig. 2. (001) projection of the ordered model (space group $P6_4$) of (a) SrDH and (b) CaDH used for ORD calculations.

Table 1. Atomic coordinates of SrDH and CaDH in space group $P6_4$

	x	y	z
SrDH			
Sr	0	0	$\frac{1}{2}$
S	0.3096	0.9349	0.4978
O1	0.264	0.033	0.5610
O2	0.273	0.037	0.4357
O3	0.197	0.673	0.4939
O4	0.8055	0.5502	0.6243
O5	0.5502	0.8055	0.7090
CaDH			
Ca	0	0	$\frac{1}{2}$
S	0.3053	0.9362	0.4962
O1	0.261	0.027	0.5633
O2	0.274	0.043	0.4310
O3	0.184	0.667	0.4955
O4	0.8115	0.5653	0.6271
O5	0.5653	0.8115	0.7062

Table 2. Calculated (using the program of DG) and observed values for the refractive indices and optical rotatory dispersion ρ ($^{\circ}\text{mm}^{-1}$) in dextrorotatory $\text{SrS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$

Input isotropic polarizabilities (\AA^3)	Observed	Calculated
$\alpha_{\text{Sr}} = 1.593$	$\rho = 4.59$	$\rho = 4.60$
$\alpha_{\text{O(S)}} = 1.163$	$n_o = 1.5358$	$n_o = 1.5358$
$\alpha_{\text{O(W)}} = 1.929$	$n_e = 1.5310$	$n_e = 1.5310$

Table 3. Calculated (using the program of DG) and observed values for the refractive indices and optical rotatory dispersion ρ ($^{\circ}\text{mm}^{-1}$) in dextrorotatory $\text{CaS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$

Input isotropic polarizabilities (\AA^3)	Observed	Calculated
$\alpha_{\text{Ca}} = 0.59$	$\rho = 2.86$	$\rho = 2.84$
$\alpha_{\text{O(S)}} = 1.195$	$n_o = 1.5580$	$n_o = 1.5580$
$\alpha_{\text{O(W)}} = 1.977$	$n_e = 1.5468$	$n_e = 1.5467$

latter occurring for pairs of atoms AB , CD , EF , GH , IJ and KL . Although these bonds are particularly long, they are inclined close to $[001]$, and it is the shorter bonds BC , DE , FA , HI , JK and LG that are important for the ORD displayed. As a result of the long bonds breaking up the helix, the ORD is observed to be small, despite the large polarizabilities. The orientations of the O4 and O5 polarizability ellipsoids on the helices are mainly determined by their interaction with the Sr atoms: if the same input polarizability volumes are attributed to O(S) and O(W) [$\alpha_{\text{O(S)}} = 1.163$ and $\alpha_{\text{O(W)}} = 1.929 \text{ \AA}^3$] but a very small value is given to Sr ($\alpha_{\text{Sr}} = 0.1 \text{ \AA}^3$), the calculated ORD changes sign and its value becomes $\rho = -2.57^{\circ}\text{mm}^{-1}$. This negative ORD can be explained again from the orientations of the O(W) polarizability ellipsoids on the helices considered (Fig. 4a). The polarizability ellipsoids of the atoms BDF and HJL are now oriented tangentially to the helix, while ACE and GIK have changed their

orientation now pointing outwards from the helix axis with only a slightly larger radial component. As, according to GS, the light should rotate now in the same sense as the helices, a negative ORD results. The polarizability ellipsoids are less anisotropic (mainly for O4 atoms) which may explain the smaller magnitude of the ORD obtained. The Sr—O(W) interaction determines the orientation as well as the anisotropy of the atomic polarizability ellipsoids on the helices (Figs. 4a–h). An increase of the Sr polarizability volumes (Figs. 4f–h) makes the water oxygen polarizability ellipsoids more anisotropic and forces them to point towards the helix axes, and an increase in the positive value of ORD can be observed. Decrease in the Sr polarizability (Figs. 4d–a) weakens the Sr—O(W) interaction and, as a result, the tangential component of the polarizability ellipsoids increases (mainly for the O4 atoms which rapidly become oriented tangentially to the helices) and their anisotropy becomes smaller. The ORD then decreases in magnitude and eventually changes sign. In Fig. 5 the variation of the (calculated) ORD with the Sr polarizability volume, corresponding to Figs. 4(a–h), is plotted.

The smaller ORD displayed by CaDH, compared with SrDH, results then from the smaller polarizability volumes of the Ca atoms. As a result of the weaker Ca—O(W) interaction, the O4 polarizability

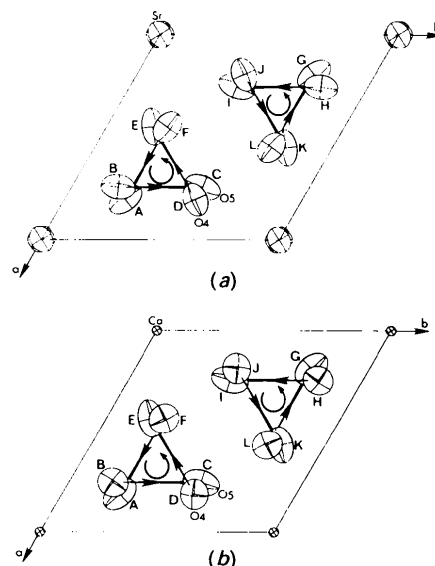


Fig. 3. (001) projection of the (a) SrDH and (b) CaDH structures showing only the metal and water oxygen polarizability ellipsoids as determined by the DG program for fitted values of ORD and refractive indices (Tables 2 and 3). The arrows denote the two $RS2/3$ helices (entities $ABCDEF$ and $GHIJKL$) of O(W) identified as the structural origin of the ORD. The polarizability ellipsoids are drawn on an arbitrary scale.

ellipsoids now have a larger tangential component (Fig. 3*b*). As the O5 polarizability ellipsoids are oriented radially on the helices, a small but positive ORD is measured.

The fundamental role played by the metal atoms in the ORD displayed by some materials has already been pointed out in $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ (Thomas & Gomes, 1989). Here too, although there are very different structural helices, the ORD was strongly dependent on the interactions between the Ba and water O atoms.

According to the predictions of GS and as verified for many compounds (GS; Stadnicka, Glazer & Koralewski, 1987, 1988), the polarizability and thermal ellipsoids are in general perpendicular to one another, showing that anisotropic polarizabilities tend to be largest in directions where the thermal vibrations are smallest. This was found to be the case for the water oxygens in SrDH and CaDH (Figs. 6*a* and 6*b*). The eigenvalues and eigenvectors for thermal and polarizability ellipsoids are listed in Tables 4 and 5 for SrDH and CaDH respectively.

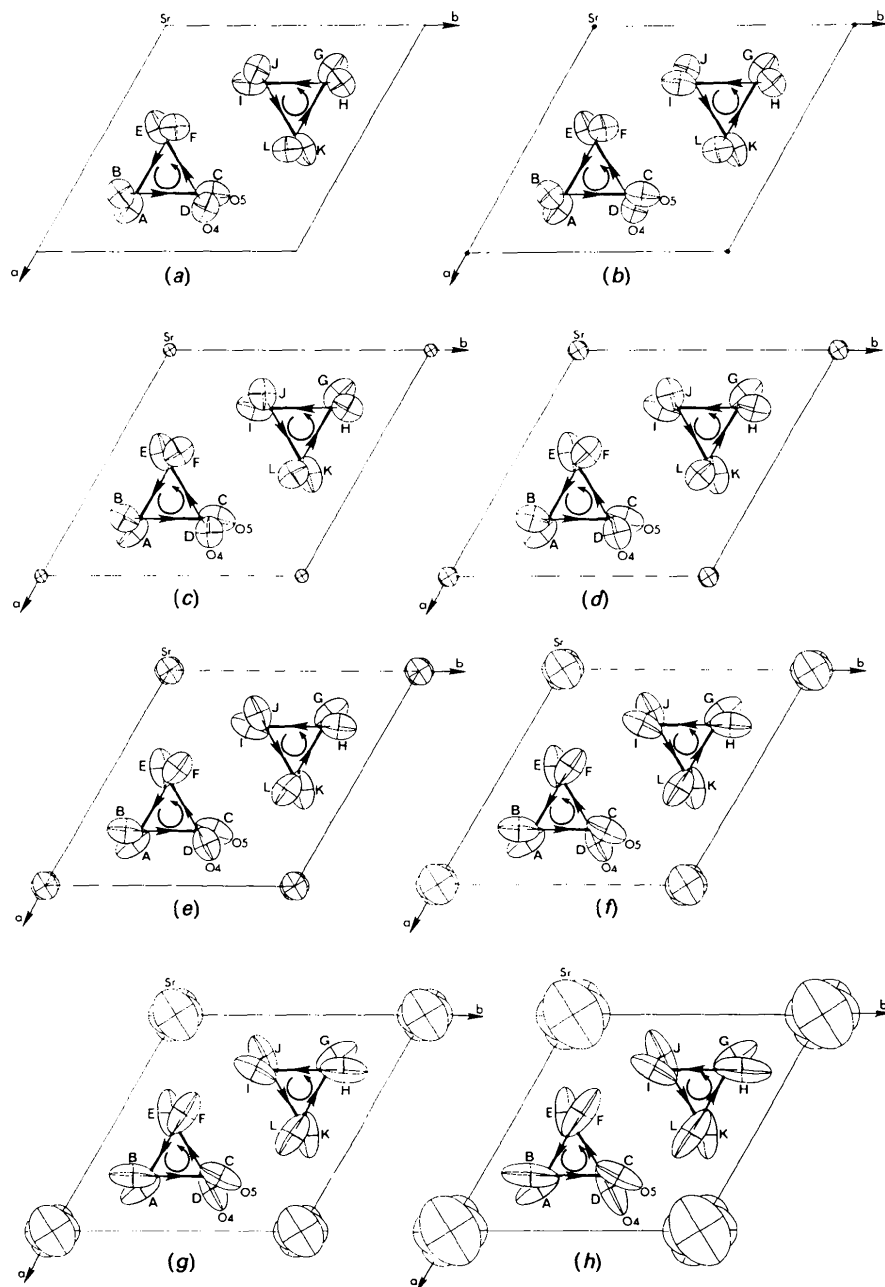


Fig. 4. Polarizability ellipsoids for Sr and O(*W*) atoms showing the effect of increasing [(*f*) to (*h*)] and decreasing [(*d*) to (*a*)] Sr polarizability volumes compared to the value in (*e*). The polarizability volume of O(*S*) and O(*W*) are constant [$a_{\text{O}(\text{S})} = 1.163$ and $a_{\text{O}(\text{W})} = 1.929 \text{ \AA}^3$] and the input Sr volume polarizabilities and calculated ORD are (a) $\alpha_{\text{Sr}} = 0.1 \text{ \AA}^3$, $\rho = -2.57^\circ \text{ mm}^{-1}$; (b) $\alpha_{\text{Sr}} = 0.3 \text{ \AA}^3$, $\rho = -1.88^\circ \text{ mm}^{-1}$; (c) $\alpha_{\text{Sr}} = 0.8 \text{ \AA}^3$, $\rho = 0.15^\circ \text{ mm}^{-1}$; (d) $\alpha_{\text{Sr}} = 1.15 \text{ \AA}^3$, $\rho = 1.89^\circ \text{ mm}^{-1}$; (e) $\alpha_{\text{Sr}} = 1.593 \text{ \AA}^3$, $\rho = 4.59^\circ \text{ mm}^{-1}$; (f) $\alpha_{\text{Sr}} = 2.15 \text{ \AA}^3$, $\rho = 9.02^\circ \text{ mm}^{-1}$; (g) $\alpha_{\text{Sr}} = 2.60 \text{ \AA}^3$, $\rho = 13.77^\circ \text{ mm}^{-1}$; (h) $\alpha_{\text{Sr}} = 3.20 \text{ \AA}^3$, $\rho = 22.46^\circ \text{ mm}^{-1}$.

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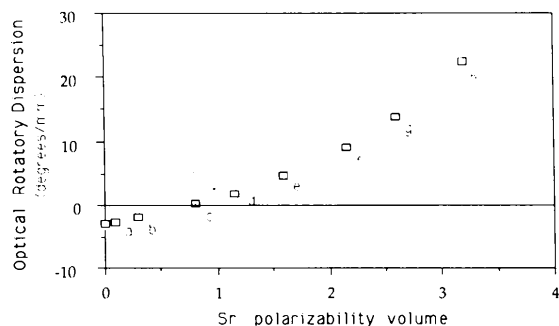


Fig. 5. ORD as a function of Sr polarizability volume [$\alpha_{O(S)} = 1.163 \text{ \AA}^3$ and $\alpha_{O(W)} = 1.929 \text{ \AA}^3$].

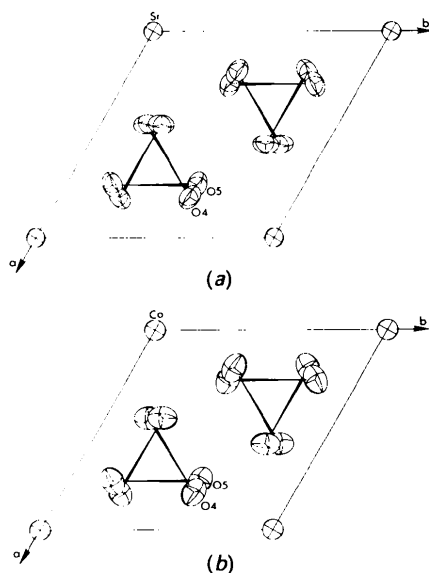


Fig. 6. Thermal ellipsoids of metal and water O atoms for (a) SrDH and (b) CaDH.

Table 4. Eigenvalues and eigenvectors of thermal and polarizability ellipsoids for Sr and O(W) atoms in $\text{SrS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$

Eigenvalue		Eigenvector		
Thermal eigenvalues (\AA^2) and eigenvectors				
O(W)	0.0159	0.5126	0.8224	0.0247
	0.0273	0.6805	-0.2137	-0.7009
	0.0371	0.5236	-0.5273	0.6692
Polarizability eigenvalues (\AA^3) and eigenvectors				
O4	2.4379	0.1896	-0.1619	0.9684
	3.8267	0.9481	-0.2262	-0.2235
	4.2346	0.2553	0.9605	0.1106
O5	2.4618	0.0765	-0.0722	0.9945
	3.8223	-0.1357	0.9873	0.0821
	4.3346	0.9878	0.1412	-0.0658

Table 5. Eigenvalues and eigenvectors of thermal and polarizability ellipsoids for Ca and O(W) atoms in $\text{CaS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$

Eigenvalue		Eigenvector		
Thermal eigenvalues (\AA^2) and eigenvectors				
O(W)	0.0235	0.6002	0.7363	-0.3126
	0.0276	0.0928	-0.4525	-0.8871
	0.0433	0.7945	-0.5034	0.3397
Polarizability eigenvalues (\AA^3) and eigenvectors				
O4	2.6087	0.2273	-0.0946	0.9692
	4.0313	0.7953	0.5923	-0.1287
	4.3110	0.5619	-0.8001	-0.2099
O5	2.6472	0.0023	-0.0753	0.9972
	4.1283	0.7365	-0.6744	-0.0526
	4.3409	-0.6764	-0.7347	-0.0539

References

- BELYAEV, L. M. & PEREKALINA, Z. B. (1967). *Sov. Phys. Crystallogr.* **12**(2), 243–247.
- DEVARAJAN, V. & GLAZER, A. M. (1986). *Acta Cryst.* **A42**, 560–569.
- GLAZER, A. M. & STADNICKA, K. (1986). *J. Appl. Cryst.* **19**, 108–122.
- KLIKOVA, A. YU. & PEREKALINA, Z. B. (1976). *Sov. Phys. Crystallogr.* **21**(4), 444–447.
- MATOS GOMES, E. DE (1991a). *Acta Cryst.* **B47**, 12–17.
- MATOS GOMES, E. DE (1991b). In preparation.
- MOXON, J. & RENSHAW, A. (1990). *J. Phys. C*. In preparation.
- PAPE, C. (1867). *Ann. Phys. Chem.* **215**, 224–226.
- ROSE, H. (1910). *Neues Jahrb. Mineral Geol. Palaontol.* **29**, 53–55.
- STADNICKA, K., GLAZER, A. M. & KORALEWSKI, M. (1987). *Acta Cryst.* **B43**, 319–325.
- STADNICKA, K., GLAZER, A. M. & KORALEWSKI, M. (1988). *Acta Cryst.* **B44**, 356–361.
- TESSMAN, J. R., KATTA, A. H. & SHOCKLEY, W. (1953). *Phys. Rev.* **92**, 890–895.
- THOMAS, P. A. & GOMES, E. (1989). *Acta Cryst.* **B45**, 348–355.