position 2(*d*) (0, $\frac{1}{2}$, $\frac{1}{2}$ and $\frac{1}{2}$, $\frac{1}{2}$, 0, symmetry 2/*m*) in which the $K^+$ ion is off-centered (positioned on the binary axis, out of the mirror) and occupies, in a statistical disorder, one of the two positions related by the mirror plane and 0·41 (2) Å apart. The coordination of this ion is triangular base-prismatic, if we consider only Se—K distances less than 3·56 Å. Two of them are much shorter than the four others. The off-centering of the $K^+$ gives rise to a lengthening of some of the K—Se distances. This kind of coordination was also found in $KIn_5S_8$ (Carré & Pardo, 1983), in which, however, the $K^+$ ion remains in a mirror plane of the space group, in a different statistical disorder. The K—K distances are then longer [0·912 (12) Å].

In spite of several similarities, the $KCr_5Se_8$ and $KIn_5S_8$ compounds are not isostructural. In $KIn_5S_8$, the atoms In(1) and In(2) [which are homologues of Cr(1) and Cr(2) in $KCr_5Se_8$] are octahedrally coordinated while In(3) [homologous to Cr(3)] is only tetrahedrally coordinated. Moreover, in $KIn_5S_8$, no pseudo translation is present. Finally, the $KIn_5S_8$ structure is well defined by the stacking sequence $[\text{In(1)–octahedron–In(3)–tetrahedron–In(3')–tetrahedron}]_n$. Thus, two layers related by the [010] translation are linked by the vertices (S atoms) of the dioctahedra around In(2): the cavity is then occupied by the $K^+$ ion in the mirror plane, in a statistical disorder.

To conclude, the $KCr_5Se_8$ structure is characterized by the existence of a tunnel of Se atoms in which a $K^+$ ion occupies the site along the binary axis in a statistical disorder.

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# Refinement of the Structure of Orthorhombic Sulfur, α-$S_8$

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**Abstract.** α-Sulfur, $S_8$, $M_r = 256{\cdot}51$, orthorhombic, *Fddd*, $a = 10{\cdot}4646\ (1)$, $b = 12{\cdot}8660\ (1)$, $c = 24{\cdot}4860\ (3)$ Å, $V = 3296{\cdot}7$ Å$^3$, $Z = 16$, $D_x = 2{\cdot}067$ g cm$^{-3}$, Mo $K\alpha$, $\lambda\alpha_1 = 0{\cdot}70930$ Å, $\mu = 19{\cdot}90$ cm$^{-1}$, $F(000) = 2048$, $T = 298$ K, $R = 0{\cdot}019$, $wR = 0{\cdot}023$ for 851 reflections with $I \geq 3\sigma(I)$, $R = 0{\cdot}019$ ($wR = 0{\cdot}020$) for 506 reflections with $I \geq 3\sigma(I)$ and $(\sin\theta)/\lambda \geq 0{\cdot}481$ Å$^{-1}$. Mean structural parameters are the same for both refinements: S—S = 2·046 (3) (uncorrected) and 2·055 (2) Å (corrected for libration), S—S—S = 108·2 (6) and S—S—S—S = 98·5 (19)°.

**Introduction.** Although orthorhombic sulfur (α-S) is the most familiar form of the element and was the first to be subjected to a crystallographic analysis, it remains the least-precisely determined structure of elemental sulfur. Structural studies have been elegantly summarized by Donohue (1982), the most recent studies of α-S all being based on the data of Abrahams (1955). The lowest *R* value in the literature (0·126) is that of Pawley & Rinaldi (1972), who stated that efforts to obtain higher-quality data were in progress at that time. Since no further work on α-S has appeared to date, it must be assumed that no significantly better data set had been obtained. We report here a redetermination of the α-S structure based on a new room-temperature data set, which has resulted in a substantial improvement in the precision of the derived structural parameters.

**Experimental.** High-quality crystals of α-S were isolated from the reaction mixture of $[Fe\{C_5H_3(PPh_2)Li\}_2]$.TMED and elemental sulfur along with those of the desired product $[Fe\{C_5H_3(PPh_2)\}_2]S_3$ (Butler, Cullen, Einstein, Herring, Jagannathan & Willis, 1987). The crystals were octahedral in shape with faces of the form {111} developed, distances between parallel faces ranging from 0·31 to 0·35 mm. The unusual pale-violet

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color of the crystals is thought to result from trace amounts of a ferrocene-based impurity; the extinction coefficient of (yellow) ferrocene is about 100, while those of red and red-orange substituted ferrocenes are in the range 1000–10000, so that an upper limit of about $10^{-5}$ mole fraction of ferrocene-based impurity can be estimated (which is too small to influence other physical properties such as density). Enraf–Nonius CAD-4F diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Intensities for $\theta \leq 30°$, *hkl*: 0 to 14, −18 to 18, 0 to 34, $\omega$–$2\theta$ scan, $\omega$ scan width $(0{\cdot}65 + 0{\cdot}35\tan\theta)°$ at 1·0–10° min$^{-1}$, extended 25% on each side for background measurement, three standard reflections, variation 1%, Lp and intensity absorption corrections, transmission factors 0·54–0·65, 2407 reflections measured, 1208 unique ($R_{\text{int}} = 0{\cdot}009$), 851 with $I \geq 3\sigma(I)$, where $\sigma^2(I) = S + 4(B_1 + B_2) + [0{\cdot}04(S - 2B_1 - 2B_2)]^2$, $S$ = scan, $B_1$ and $B_2$ = background counts. Lattice constants from Cooper, Bond & Abrahams (1961) [in agreement with the more recent measurements of Wallis, Sigalas & Hart (1986)], and atomic parameters of Abrahams (1961) used as starting point of refinement. Full-matrix least squares on $F$, $w = 1/\sigma^2(F)$, scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974), locally written or locally modified versions of standard computer programs, final $R = 0{\cdot}019$, $wR = 0{\cdot}023$ for 851 reflections with $I \geq 3\sigma(I)$, $S = 1{\cdot}069$, 37 parameters, $R = 0{\cdot}037$ for all 1208 reflections,* $\Delta/\sigma = 0{\cdot}001$ (mean), 0·002 (max.), $\Delta\rho = -0{\cdot}53$ to $+0{\cdot}20$ e Å$^{-3}$. A high-angle refinement was also carried out, final $R = 0{\cdot}019$, $wR = 0{\cdot}020$ for 506 reflections with $I \geq 3\sigma(I)$ and $\theta \geq 20°$, $\Delta/\sigma = 0{\cdot}002$ (mean), 0·005 (max.). Bond lengths corrected for libration (Schomaker & Trueblood, 1968). The $R$ values of 0·019, although very low, are high relative to $R_{\text{int}}$ of 0·009, probably a result of inability to account for minor details of electron density. A careful analysis of a difference map calculated using all data and based on the parameters of the high-angle refinement was carried out in the hope that bonding and lone-pair electron densities could be identified. Unfortunately no convincing details were in evidence, the most prominent features being negative densities near the S atoms.

**Discussion.** Final atomic coordinates and anisotropic thermal parameters are given in Tables 1 and 2. There are no statistically significant differences between coordinates and thermal parameters derived from the full data and high-angle refinements, although the thermal parameters resulting from the high-angle refinement are smaller, on the average, by 1·4% than those obtained from the full data refinement. The thermal parameters are slightly lower than those reported earlier, *e.g.* 7% less than those of Pawley & Rinaldi (1972), while positional parameters and geometrical parameters (Table 3) agree to within experimental error with the previous results.

Table 1. *Final positional (fractional* × $10^5$*) and equivalent isotropic thermal parameters* (Å$^2$ × $10^3$) *with e.s.d.'s in parentheses*

| | $x$ | $y$ | $z$ | $U_{\text{eq}}$* |
|---|---|---|---|---|
| S(1) | 85584 (4) | −4733 (3) | −4854 (1) | 45 |
| | 85585 (6) | −4732 (4) | −4860 (2) | 44 |
| S(2) | 70733 (4) | −2023 (3) | 409 (2) | 45 |
| | 70723 (6) | −2031 (4) | 406 (2) | 44 |
| S(3) | 78415 (4) | 3022 (3) | 7623 (2) | 46 |
| | 78402 (6) | 3022 (4) | 7618 (2) | 45 |
| S(4) | 78596 (3) | −9232 (3) | 12947 (2) | 43 |
| | 78595 (5) | −9239 (5) | 12947 (2) | 43 |

* $U_{\text{eq}} = \frac{1}{3}$ trace (diagonalized **U**), second entry for each atom corresponds to high-angle refinement. Origin at $\bar{1}$.

Table 2. *Final anisotropic thermal parameters* ($U_{ij}$ × $10^4$ Å$^2$) *and their e.s.d.'s*

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| S(1) | 608 (2) | 396 (2) | 333 (2) | 32 (2) | 52 (2) | 80 (1) |
| | 598 (3) | 390 (3) | 326 (2) | 31 (2) | 48 (2) | 79 (1) |
| S(2) | 441 (2) | 486 (2) | 414 (2) | 99 (2) | −53 (1) | 17 (2) |
| | 439 (3) | 478 (3) | 411 (3) | 96 (2) | −51 (2) | 15 (2) |
| S(3) | 580 (3) | 370 (2) | 426 (2) | 10 (2) | 41 (2) | −90 (1) |
| | 572 (3) | 366 (3) | 424 (3) | 11 (2) | 41 (2) | −91 (2) |
| S(4) | 336 (2) | 623 (2) | 338 (2) | −18 (2) | 61 (1) | 29 (2) |
| | 332 (2) | 618 (3) | 331 (2) | −21 (2) | 58 (2) | 28 (2) |

The anisotropic thermal parameters employed in the refinement are $U_{ij}$ in the expression

$$f = f^0\exp(-2\pi^2 \textstyle\sum\sum U_{ij}h_ih_ja_i^*a_j^*).$$

Table 3. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°) *with e.s.d.'s in parentheses*

| | Full data | | High-angle data | |
|---|---|---|---|---|
| | uncorr. | corr. | uncorr. | corr. |
| S(1)–S(1′) | 2·0384 (7) | 2·050 | 2·0386 (10) | 2·050 |
| S(1)–S(2) | 2·0489 (6) | 2·056 | 2·0499 (8) | 2·057 |
| S(2)–S(3) | 2·0463 (5) | 2·057 | 2·0461 (8) | 2·056 |
| S(3)–S(4) | 2·0459 (6) | 2·054 | 2·0475 (8) | 2·056 |
| S(4)–S(4′) | 2·0444 (7) | 2·055 | 2·0438 (10) | 2·054 |
| Mean S–S | 2·046 (3) | 2·055 (2) | 2·046 (3) | 2·055 (2) |
| S(1′)–S(1)–S(2) | 108·42 (3) | | 108·38 (4) | |
| S(1)–S(2)–S(3) | 107·39 (2) | | 107·38 (3) | |
| S(2)–S(3)–S(4) | 108·01 (2) | | 108·01 (3) | |
| S(3)–S(4)–S(4′) | 108·99 (2) | | 108·99 (3) | |
| Mean S–S–S | 108·2 (6) | | 108·2 (6) | |
| S(2′)–S(1′)–S(1)–S(2) | −96·94 (4) | | −96·97 (5) | |
| S(1′)–S(1)–S(2)–S(3) | 98·85 (3) | | 98·90 (4) | |
| S(1)–S(2)–S(3)–S(4) | −100·81 (3) | | −100·82 (4) | |
| S(2)–S(3)–S(4)–S(4′) | 98·12 (3) | | 98·12 (4) | |
| S(3)–S(4)–S(4′)–S(3′) | −95·27 (4) | | −95·24 (5) | |
| Mean S–S–S–S | 98·5 (19) | | 98·5 (19) | |

Primes refer to symmetry operation $\frac{7}{4} - x$, $-\frac{1}{4} - y$, $z$. Mean values are averaged over the entire molecule, r.m.s. deviations from the mean being given in parentheses.

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* A list of structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44242 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

As a result of the higher precision of the present analysis, the differences between the individual S—S distances appear to be statistically significant. However, correction for libration improves the agreement between individual S—S distances, the mean corrected value of 2·055 (2) Å and the mean S—S—S angle of 108·2 (6)° agreeing well with the best previous values (Donohue, 1982) of 2·060 (3) Å and 108·0 (7)°. As before, the diffraction data are fitted well by a rigid-body model (r.m.s. $\Delta U_{ij} = 0{\cdot}0010$ Å$^2$), but independent internal modes are likely to be present (r.m.s. $\sigma U_{ij} = 0{\cdot}0002$ Å$^2$). A detailed discussion of these points has been given by Pawley & Rinaldi (1972), which includes discussion of the marked deviation of the solid-state structure from the $\bar{8}2m$ ($D_{4d}$) symmetry of the free-state $S_8$ molecule.

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# Trineodymium Ruthenate(V). A Rietveld Refinement of Neutron Powder Diffraction Data

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**Abstract.** $Nd_3RuO_7$, $M_r = 575{\cdot}82$, orthorhombic, *Cmcm*, $a = 10{\cdot}9042$ (6), $b = 7{\cdot}3827$ (5), $c = 7{\cdot}4963$ (4) Å, $V = 603{\cdot}47$ (9) Å$^3$, $Z = 4$, $D_x = 3{\cdot}82$ Mg m$^{-3}$, $\mu R = 0{\cdot}56$. The structure has been refined by Rietveld analysis of neutron powder diffraction data recorded at room temperature [$\lambda = 2{\cdot}5804$ (1) Å, $R_I = 4{\cdot}88$, $R_p = 8{\cdot}83$, $R_{wp} = 9{\cdot}09\%$]. The compound adopts an orthorhombic fluorite-related structure of the $La_3NbO_7$ type. One third of the Nd ions are eight-coordinated and lie in rows in the [001] direction which alternate with parallel rows of corner-linked $RuO_6$ octahedra. The remaining two thirds of the Nd ions are seven-coordinated and lie between the slabs of the $NdO_8$ and $RuO_6$ polyhedra.

**Introduction.** In a programme to investigate ceramic materials for their use as potential host lattices for the disposal of nuclear waste (Ringwood, 1978), we studied the equilibrium at 1573 K in the system BaO–$RuO_2$–$Nd_2O_3$.

In this system $Nd_2Ru_2O_7$ with the pyrochlore structure is known to exist (Bertaut, Forratana & Montmory 1959). Dixon, Marr, Lachowski, Gard & Glasser (1980) reported the presence of the orthorhombic phase $Nd_2RuO_5$ also. We were unable to prepare this compound but found a new orthorhombic phase with a higher neodymium content: $Nd_3RuO_7$. van Berkel & IJdo (1986) describe this compound with space group *Cmcm* as a superstructure of the cubic fluorite structure with $a_{\rm orth} \simeq 2a_{\rm c}$, $b_{\rm orth} \simeq c_{\rm orth} \simeq \sqrt{2}a_{\rm c}$ and suggest the same structure as that found for $La_3NbO_7$, determined from X-ray powder diffraction (Rossell, 1979).

A very precise structure determination is necessary for an interpretation of the magnetic properties of $Nd_3RuO_7$.

**Experimental.** The system was prepared from 99·9% $Nd_2O_3$, ignited at 1273 K; $RuO_2$ was prepared from fine metal (99·99%) at 1073 K in air. The mixture was heated in an alumina crucible in a vacuum-sealed quartz tube according to:

$$Nd_2Ru_2O_7 + 2Nd_2O_3 + \tfrac{1}{2}O_2 \rightarrow 2Nd_3RuO_7.$$

The oxygen was added as $KClO_3$ in a separate crucible. X-ray powder diffraction patterns were obtained with a Philips PW 1050 diffractometer.

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