Table 2(*b*) shows, the uranium-atom position corresponded remarkably well to the correct one. Reeke & Lipscomb (1969) have also reported that the tangent formula works at 6·0 Å.

The 8·0 Å data, however, did not give as good a result. Various attempts at multi-solution phasing with ΔE greater than 1·0 and 0·5 produced a number of phase sets, only two of which had R less than 0·40. The less consistent of the two had the lower R of 0·38, by nearly 0·02, and was the better solution, as judged by the ΔE map. Fig. 1(*b*) [Table 2(*b*)] shows that the uranium atom, determined at 8·0 Å resolution was over 4 Å away from its true position. The ΔE map did not show the good peak discrimination encountered earlier; the strongest spurious peak had half the strength of the correct one. It is possible that significant errors in the ΔE values at this low resolution were to some extent responsible for these results.

It thus seems that direct three-dimensional phasing of ΔF data sets can reliably locate heavy atoms in biological macromolecules, even when only 5 or 6 Å resolution data are available, provided that the individual heavy atoms are well resolved. Not too much reliance can be placed on lower-resolution results. As Steitz (1968) has pointed out, these methods could be of considerable use in the structure analysis of molecules with multiple heavy-atom binding sites. Where high-symmetry space groups are involved, Patterson map interpretation becomes especially difficult and statistical phasing to locate heavy atoms is particularly advantageous.

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La_2O_2S structure refinement and crystal field.*

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Parameters on the structure of La_2O_2S have been refined by the least-squares method using 396 Mo $K\alpha$ intensity data. In space group $P\bar{3}m1$, the La^{3+} ion occupies 3(*m*) sites surrounded below by three S^{2-} ions (3·037 Å) and above by three O^{2-} ions (2·424 Å) and one axial O^{2-} ion (2·423 Å). A new crystal-field analysis has been performed using this data.

Introduction

The rare-earth oxysulfides activated with trivalent rare-earth ions form an important technological class of materials with high luminous efficiency (Struck & Fonger, 1971; Dobrov & Buchanan, 1972). In particular, neodymium-activated lanthanum oxysulfide, La_2O_2S:Nd, has received some attention as a promising new high-gain laser material and, hence, has stimulated studies on the growth of the required single crystals (Alves, Buchanan, Wickersheim & Yates, 1971; Baughman, 1973). The simplicity of the crystal structure as well as the many various isomorphous members and/or dopants makes the material ideal for analysis of crystal-field parameters (Sovers & Yoshioka, 1969; Newman & Stedman, 1971). Unfortunately, only approximate atomic parameters obtained by the powder method were available (Wyckoff, 1960) leading Newman & Stedman to obtain values for superposition model parameters (in their crystal-field analysis) which were difficult to interpret. Crystal structure parameters determined on 1 wt.% Nd doped La_2O_2S material kindly supplied by Baughman are reported in this note.

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Experimental details and results

A single-crystal specimen was ground to a radius of 0·0121 cm. The specimen was examined by long-exposure photographic methods to insure that $P\bar{3}m1$ is the correct space group. Lattice constants were determined to be $a_0 = 4{\cdot}049$ (1) and $c_0 = 6{\cdot}939$ (2) Å by measurements made on a Picker diffractometer. The θ–2θ scan technique and a scintillation detector employing pulse-height discrimination were used to measure a complete hemisphere (to 95° 2θ) of Mo $K\alpha$ intensity data. A unique data set of 396 intensities was obtained by averaging the symmetry-related values provided the differences were less than $\sigma_{ave}/\sqrt{n}$, where σ_{ave} is the average σ for n measurements with the usual definition of $\sigma = (N_{SC} + K^2 N_B)^{1/2}$, where N_{SC}, N_B and K are the total scan count, background counts and the time ratio of the scan to background respectively. In the few instances where an intensity did not agree to within this criterion, it was discarded and averaging was performed on the remaining intensities. All reflections were considered observed. Spherical absorption corrections (μ[Mo $K\alpha$] = 190 cm^{-1}) were ap-

plied from Table 5.3.6B of *International Tables for X-ray Crystallography* (1969). Initial parameters were taken from Wyckoff and the intensity data subjected to least-squares refinement. The function, $w(F_o - F_c)^2$, was minimized with $w = n/\sigma^2_{ave}$ and with structure factors calculated using scattering factors taken from Table 3.3.1A and 3.3.1B and dispersion corrections from Table 3.3.2C of *International Tables for X-ray Crystallography* (1962). The residual $R = \sum||F_o| - |F_c||/\sum|F_o|$ was 0·038 and 0·031, respectively, using isotropic and anisotropic thermal parameters. The positional and thermal parameters, observed and calculated structure factors, and interatomic separations are given in Tables 1, 2 and 3 respectively.

In this structure, the rare-earth ion is located on a threefold axis with a triangle of three sulfide ions below it (3·037 Å) and a triangle of three oxide ions (2·424 Å) and one axial oxide ion (2·423 Å) above it. The sulfide ion is surrounded by two triangles (one above and one below) of three oxide ions at 2·481 Å and two triangles of rare-earth ions while the oxide ion is surrounded below by one axially located rare-earth ion and a triangle of three oxide ions (2·940 Å) and above by a triangle each of sulfide and rare-earth ions. These separations are slightly different from the corresponding values (3·086, 2·430 and 2·389 Å respectively) calculated from the parameters in Wyckoff. The associated changes in angular coordination are, however, in the correct direction to yield improved accuracy for the intrinsic parameters of the sulfide ion determined by the superposition model in the analysis of the crystal field in rare-earth oxysulfides by Newman & Stedman.

Table 1. *Positional and thermal parameters for* La_2O_2S:Nd

	x	y	z	u_{11}	u_{33}
S	0	0	0	0·29 (6)	0·37 (8)
La	$\frac{2}{3}$	$\frac{1}{3}$	0·27929 (6)	0·15 (2)	0·31 (2)
O	$\frac{2}{3}$	$\frac{1}{3}$	0·6287 (8)	0·17 (9)	0·19 (14)

Table 2. *Observed and calculated structure factors for* La_2O_2S

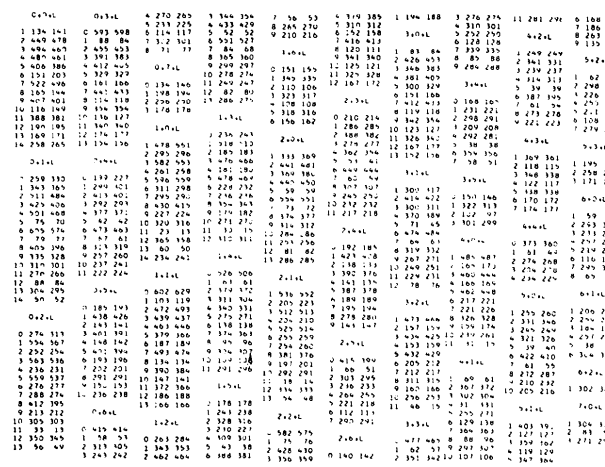

Table 3. *Interatomic separations and angles for* La_2O_2S:Nd

La–O′	2·423 (6) Å	S-----La–S	83·62 (1)°
La–O″	2·424 (2)	O′----La–S	129·66 (1)
La–S	3·037 (1)	O′-----La–O″	74·7 (1)
La–La	3·853 (1)	O″---La-O″	113·29 (9)
S--O′	3·481 (1)	O′----S--La	87·47 (7)
O′–O″	2·940 (6)	La----S--La	83·62 (1)
		O′----S--O′	71·14 (8)
		La----S--O′	43·00 (2)

To demonstrate this the angles given in Table 3 are used to recalculate the intrinsic parameters for the system La_2O_2S:Eu. The method of analysis has been described by Newman & Stedman and the experimental crystal-field parameters were obtained by Sovers & Yoshioka. The following crystal field parameters representing the contributions of single oxygen or sulphur ligands are obtained:

$$\bar{A}_4(O) = 88{\cdot}2\ cm^{-1} \qquad \bar{A}_6(O) = 18{\cdot}9\ cm^{-1}$$
$$\bar{A}_4(S) = 18{\cdot}8\ cm^{-1} \qquad \bar{A}_6(S) = 5{\cdot}1\ cm^{-1}.$$

The main difference between these parameters and those determined by Newman & Stedman is the much reduced value of $\bar{A}_4(S)$ (originally given as 46·9 cm^{-1} for the Gd_2O_2S host). The ratio $\bar{A}_4(S)/\bar{A}_6(S) = 3{\cdot}7$ is now very similar to that found in other systems. Low values of the sulphur parameters are consistent with the large La–S separations in this crystal. These results show that accurate structural information is an essential prerequisite for obtaining reliable intrinsic parameters using the superposition model.

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