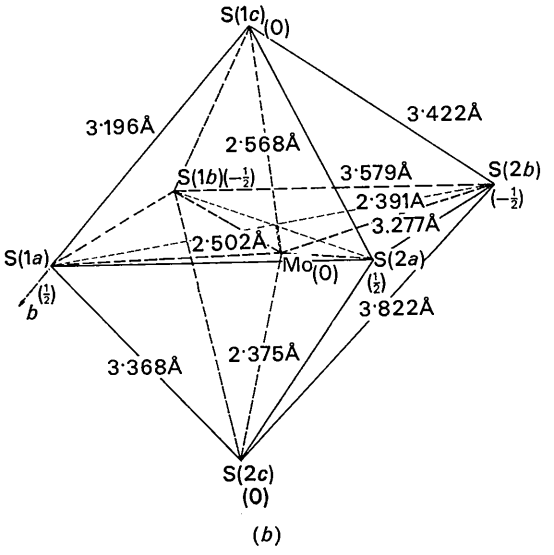

(*b*)

Fig. 2 (*cont.*)

out to provide an estimate of the absorption correction. The ratio (maximum intensity/minimum intensity) was expected to be about 1·3 ($\mu_{Mo\ K\alpha}=57$ cm^{-1}). Instead, we observed for 020, $I_{max}/I_{min}=2{\cdot}56$, and for 040, $I_{max}/_{min}=2{\cdot}16$. This deviation from the expected value, together with the clearly visible splitting of the reflexions into $K\alpha_1$–$K\alpha_2$-peaks at a θ as low as 20°, suggested that the crystal was almost perfect, and that the intensities were affected by primary extinction. The same was also observed in the structure analyses of the MNb_3S_6 series (M = Mn, Fe, Co, Ni; Anzenhofer, van den Berg & Helle, 1968) and in this case a correction procedure was applied which led to very good results. This therefore encouraged us to use the same correction procedure for the $CoMo_2S_4$ intensity data. Essentially this meant an extrapolation of the intensities, I, to values which would have been measured at the azimuth angle, where $I=I_{max}$. The correction factor was derived from the azimuthal scans.

The refinement was started in $C2/m$ with the structure model derived by van den Berg (1968). After a few cycles, the conventional R index had dropped to 16·2%. From this point onwards 14 poorly determined structure factors were omitted; also individual anisotropic temperature factors were introduced into the subsequent refinement cycles, which finally brought R down to 8·7%.

The next problem was to verify the space group $C2/m$. We modified the structure parameters to meet the specific symmetry requirements of Cm and $C2$, respectively, and refined both models. Both models clearly moved towards the $C2/m$ model, finally terminating with a singularity in the matrix when the two models approached values of structure parameters which are fixed in $C2/m$. So the space group was verified as $C2/m$. The final structure parameters are presented in Table 1 together with the estimated standard deviations. Fig. 2(*a*) and (*b*) shows the distorted sulphur octahedra about the Co and Mo atoms respectively. Bond lengths and angles are included to give the shape and distortion of the octahedra. A discussion of the $CoMo_2S_4$ structure and its relation to the magnetic properties has been presented by van den Berg (1968).

A list of the structure factors involved in the refinement calculations may be obtained on request.

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Table 1. *Final structure parameters of* $CoMo_2S_4$

If parameters are not fixed by space group symmetry, their standard deviation in the last decimal figure is given between brackets. Space group symmetry requires $\beta_{12}=\beta_{23}=0$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{13}
Co	0	0	0	0·0010 (3)	0·037 (4)	0·012 (2)	0·0009 (4)
Mo	0·2569 (1)	0	0·2043 (3)	0·0003 (2)	0·052 (3)	0·005 (1)	0·0002 (2)
S(1)	0·3622 (3)	0	0·7016 (8)	0·0010 (3)	0·027 (4)	0·006 (2)	0·0005 (5)
S(2)	0·1045 (3)	0	0·7679 (8)	0·0010 (3)	0·026 (4)	0·007 (2)	0·0030 (5)

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Further refinement of the structure of WO_3.

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The structure of WO_3, previously determined from neutron diffraction data, has been further refined with the use of improved experimental and computational techniques. Standard deviations of position parameters were reduced by an average factor of 4·8.

Recently the structure of WO_3 was determined from neutron powder diffraction data (Loopstra & Boldrini, 1966). Since this determination was completed the neutron powder diffraction technique has been improved by the use of a wavelength of about 2·6 Å (Loopstra, 1966). Moreover, the least-squares refinement method based on peak profiles was

Table 1. *Comparison of positional coordinates of* WO_3

	From present refinement			Loopstra & Boldrini (1966)		
	x/a	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
W(1)	0·2465 (16)	0·0269 (14)	0·2859 (9)	0·254 (6)	0·037 (5)	0·282 (5)
W(2)	0·2538 (17)	0·0353 (13)	0·7807 (10)	0·250 (9)	0·023 (6)	0·784 (5)
O_{x1}	0·0025 (13)	0·0350 (15)	0·2106 (8)	0·005 (5)	0·042 (5)	0·211 (4)
O_{x2}	0·9974 (13)	0·4636 (15)	0·2161 (8)	0·993 (6)	0·474 (5)	0·218 (5)
O_{y1}	0·2840 (7)	0·2605 (13)	0·2848 (7)	0·288 (3)	0·262 (6)	0·286 (3)
O_{y2}	0·2099 (8)	0·2568 (15)	0·7318 (7)	0·211 (3)	0·259 (8)	0·730 (3)
O_{z1}	0·2827 (10)	0·0383 (8)	0·0046 (7)	0·292 (6)	0·043 (5)	0·008 (4)
O_{z2}	0·2856 (10)	0·4840 (10)	0·9944 (6)	0·279 (7)	0·487 (6)	0·993 (3)

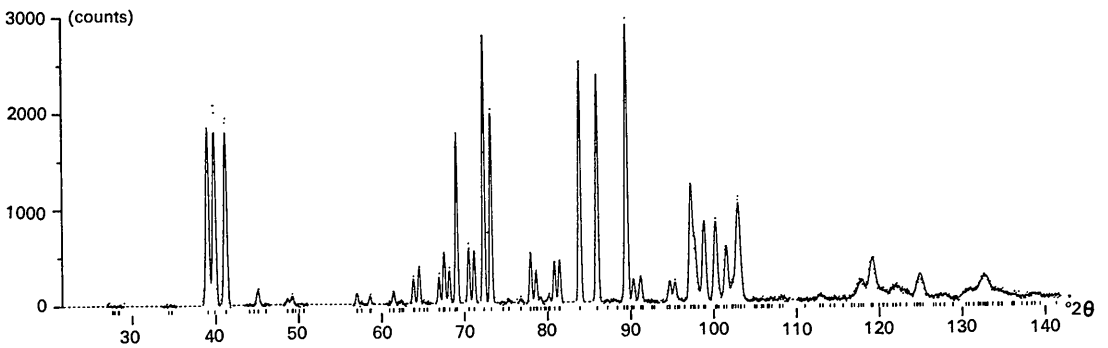

Fig. 1. Powder pattern of WO_3. The dots indicate the observed intensities, the full line the calculated pattern. Positions of Bragg peaks have been marked with vertical dashes.

introduced (Rietveld, 1967). To show the combined effect of these two developments, the structure of WO_3 has been refined again.

A fresh sample was prepared in the same fashion as previously (Loopstra & Boldrini, 1966). From X-ray diffractometer data, obtained with Cu $K\alpha$ radiation, cell constants were determined to be $a=7{\cdot}306$ (1), $b=7{\cdot}540$ (1), $c=7{\cdot}692$ (1) Å, and $\beta=90{\cdot}881$ (5)°. Neutron data were collected with a wavelength of 2·5705 (5) Å from a Cu(111) monochromator. Slits of 10′ divergence were inserted between the reactor and the monochromator, and in front of the BF_3 detector. Second and higher order reflexions were not observable. Intensities were collected over a range up to $\sin\theta/\lambda=0{\cdot}369$, comprising 178 independent reflexions.

In the least-squares calculations the following parameters were refined: the position parameters (24), a scale factor, an overall temperature factor, the scattering length of tungsten relative to that of oxygen, the zero point of the 2θ scale, the unit-cell constants (4), and the halfwidth parameters P, Q, and R from the relation:

$$b^2_\theta = P\tan^2\theta + Q\tan\theta + R\,,$$

where b is the width at half maximum of a Bragg peak at angle θ. This constitutes a total of 35 least-squares parameters to fit the calculated to the observed diffraction profile.

Fig. 1 shows the resulting agreement between the observed and computed patterns. In Table 1 the position parameters resulting from the present and the previous refinement are given for comparison. Of the 24 position parameters, 17 are equal to those of the previous set within the standard deviation, 4 within $1{\cdot}6\sigma$, and 3 differ by about 2σ. Most notable of the latter are the y parameters of the tungsten atoms which agree much more closely than on the previous occasion with the values given by Tanisaki (1960).

For the ratio of the scattering lengths, b_W/b_O, the value 0·846 (5) was found from the refinement. Taking $b_O=0{\cdot}577\times10^{-12}$ cm this leads to $b_W=0{\cdot}488\times10^{-12}$ cm. As b_O is variously quoted as being between 0·577 (4) (Willis, 1963) and $0{\cdot}577\,(10)\times10^{-12}$ cm (Valentine, 1968) it is not possible to indicate uniquely the standard deviation in the value of b_W.

It was mentioned by Rietveld (1967) that a refinement with the profile method based on the same data as that used by Loopstra & Boldrini (1966) led to an improvement in the standard deviations by an average factor of 2·3. For the present set of coordinates this factor is 4·8. The difference is a result of the utilization of a wavelength of 2·57 Å and of improvements in the refinement, in particular the inclusion of cell parameters, zero point, and halfwidth parameters in the least squares refinement.

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