portion shown filled tetrahedra sit on empty octahedra, and empty tetrahedra sit on filled octahedra, as can be confirmed by comparing the occupation of the tetrahedral site plane $(h-2K_0)_{\text{mod } 4}=5/2$ with that of the octahedral site plane $(h-2K_0)_{\text{mod } 4}=1$.

The olivine structure, which is similarly constructed, is shown in Fig. 10.

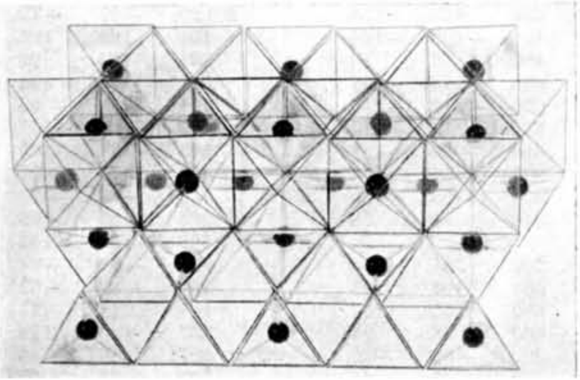

Fig. 10. Interstitial model of olivine.

In these models the tetrahedrally surrounded ions are represented by red, the octahedrally surrounded ions by blue spheres.

The interstitial models have the advantage of flexibility, since they are self-supporting and do not need interlocking mechanisms. The rods supporting the spheres actually represent the anion–cation bonds, the corners at which all edges converge, the anions, so that the structures owe their support to physically meaningful elements. Therefore these models can be used to show many crystal structures and, especially, the relationships between these structures. They are invaluable for deriving and checking the distribution patterns.

The authors are indebted to Mr Ralph Casale for his assistance and guidance in constructing the four types of modules, and to Mr Stuart Bemis for making the photographs shown in Figs. 3 through 10.

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The Crystal Structure of $KReO_4$

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Single crystals of $KReO_4$ have been examined by means of X-ray diffraction in order to determine the location of oxygen atoms in the unit cell. The unit-cell dimensions have been redetermined and found to be:

$$a=5\cdot680\pm0\cdot002,\ c=12\cdot703\pm0\cdot006\ \text{Å}\ .$$

The space group is $I4_1/a$ with 4 K and 4 Re in special positions and 16 O in general positions corresponding to $x=0\cdot131$, $y=0\cdot041$, $z=0\cdot210$. Oxygen atoms form nearly regular tetrahedra around Re. The Re–O separation suggests considerable double bond character for this bond.

Introduction

Shortly after the isolation of rhenium, Broch (1929) examined $KReO_4$ powder with Cu $K\alpha$ radiation and proposed that the salt is isomorphous with scheelite, $CaWO_4$. The present work was begun to determine the locations of the oxygen atoms in $KReO_4$, for which purpose diffraction by single crystals is required.

Experimental procedure

Pure $KReO_4$, obtained from the Department of Chemistry of the University of Tennessee, was used to prepare a water solution from which tetragonal octahedra were deposited on slow evaporation of the solvent. The specimen used for b-axis rotation had a length of 115·5 microns; its maximum cross-section was a square with side 63·0 microns. For c-axis rotation the crystal selected had corresponding dimensions of 76·1 microns and 34·4 microns. For both crystals, diffraction of Zr-filtered Mo $K\alpha$ radiation was recorded by the Weissenberg and precession methods.

Kodak No-screen and Blue Brand film, six sheets in depth, were employed for the recording of equatorial Weissenberg photographs. Intensities were estimated visually by comparison with timed exposure scales produced by the diffracting crystal. Since the small Bragg angle of (101) prevented its being recorded by the Weissenberg camera, timed ($h0l$) precession photographs furnished an estimate of the (101) intensity, intercomparison of a number of reflections recorded by both precession and Weissenberg methods making it possible to put this estimate on the same scale as the main body of ($h0l$) intensity results.

Crystals ground to 300 mesh were used to obtain back-reflection powder patterns with Ni-filtered Cu $K\alpha$ radiation and a Philips parafocusing camera of 60 mm. radius. Sample oscillation and camera evacuation were employed. The diffraction record was made on Kodak No-screen film, from one side of which emulsion was removed after exposure.

Unit cell and space group

The single crystal photographs, which can be indexed on a tetragonal basis, exhibit only reflections for which $h+k+l=2n(hkl)$, $l=4n(00l)$, and $h, k=2n(hk0)$, determining the space group as No. 88 $I4_1/a$ and, thus, confirming Broch's (1929) proposal. Precession photographs showed that the unit cell is somewhat larger than originally estimated by Broch (1929). The back-reflection powder pattern described above provided twenty-four lines with Bragg angles greater than 60°, nine of these corresponding to $K\alpha_2$ reflections. Four lines were available in the range 78–85°. Cohen's (1935) reduction of the observations yields the values:

$$a=5{\cdot}680\pm0{\cdot}002, \quad c=12{\cdot}703\pm0{\cdot}006\ \text{Å}\ .$$

Since the standard deviations for a and c were 0·001 and 0·003 Å respectively, these limits of error correspond to a probability of 95% that the lattice constants lie within the indicated limits (Jette & Foote, 1935). The unit-cell size, with the experimental density of 4·38 g.cm.$^{-3}$ (Smith & Long, 1948), shows that the unit cell contains four $KReO_4$, a feature consistent with the space group.

Determination of the structure

Re and K must necessarily occupy the 4(a) and 4(b) positions (*International Tables*, 1952) of the space group. These metal atoms contribute to the scattering only under the special restriction $2k+l=2n+1$ or $4n$. Thus spectra for which $2k+l=2(2j+1)$ must arise from oxygens alone. These spectra indicate that the oxygens occupy the 16(f) general positions (*International Tables*, 1952), since observed reflections such as (114) and (402) are not allowed if 8(c), 8(d), or 8(e) is used.

Lorentz-polarization and absorption corrections were used to obtain from the observed intensities quantities proportional to the magnitude of F_o. The latter correction, made appreciable by the strong absorption in $KReO_4$, was obtained by the method of Howells (1950). The large scattering power of the atoms in fixed positions makes sign determination straightforward for all structure factors except three arising

Table 1. *Observed and calculated structure factors*

hkl	F_o	F_c	hkl	F_o	F_c
200	229	245	6,0,12	−91	−93
220	−249	−256	8,0,12	−63	−67
240	198	185	0,0,16	105	103
260	−131	−137	2,0,16	114	107
280	80	82	4,0,16	97	90
400	189	193	6,0,16	58	70
420	−218	−210	0,0,20	57	75
440	154	134	2,0,20	−67	−72
460	−108	−104	101	129	164
480	76	80	301	105	92
600	124	137	501	103	102
620	−112	−115	701	62	65
640	117	114	103	−166	−147
660	−90	−84	303	−121	−116
800	84	94	503	−74	−77
820	−98	−89	703	−68	−75
840	81	78	105	−115	−98
			305	−135	−132
200	221	245	505	−98	−89
400	194	193	705	−60	−63
600	132	137	107	114	97
800	98	94	307	125	118
202	−52	−29	507	80	84
402	27	25	707	55	60
004	−223	−246	109	112	117
204	−242	−276	309	104	90
404	−188	−192	509	60	69
604	−154	−128	709	55	63
804	−90	−89	1,0,11	−97	−98
206	−18	−1	3,0,11	−78	−74
008	204	199	5,0,11	−68	−73
208	211	206	7,0,11	−67	−53
408	165	156	1,0,13	−88	−83
608	106	113	3,0,13	−59	−69
808	80	79	5,0,13	−58	−66
0,0,12	−193	−175	1,0,15	69	73
2,0,12	−146	−134	3,0,15	53	66
4,0,12	−124	−117	1,0,17	52	60

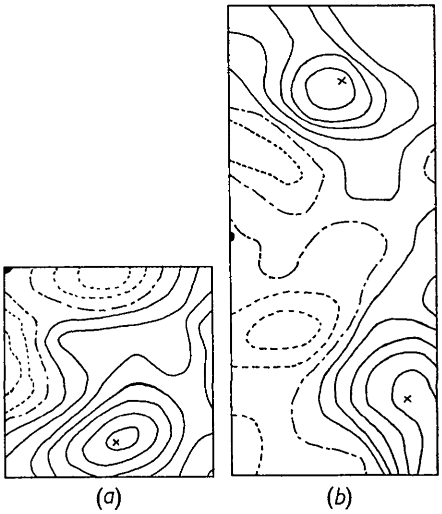

Fig. 1. Observed electron density less calculated metal atom contributions for $\frac{1}{4}\times\frac{1}{4}$ unit cell projected on (001) in (a) and on (010) in (b). Contours are drawn at intervals of 2 e.Å^{-2}. Dotted contours represent negative values; dash-dot contour represents zero density. Crosses mark locations of oxygen atoms. Quarter solid circle in (a) and half solid circle in (b) indicate potassium–rhenium and rhenium locations respectively.

from scattering by oxygen alone. To obtain initial estimates of x and y for oxygen, the projected density difference function

$$4A^{-1}\sum_{h>0}\sum_{k>0} G(h,k)\sin 2\pi hu \sin 2\pi kv$$

with

$$G(h,k) \equiv (\delta_{hk}-1)[F_o(hk0)-(-1)^{(h+k)/2}F_o(kh0)]$$

was calculated. Coordinates of the oxygen peak were used as estimated x and y. From the peak height, the temperature factor for oxygen was estimated. Initial estimate of z was obtained from $F_o(h0l)$ by trial.

Refinement of the parameters was effected by successive F_o-F_c syntheses (Lipson & Cochran, 1953). The Re atom scattering factors required for the calculations were interpolated for Re^{+3} from Thomas–Fermi values. Hartree–Fock values for K^+ and O^- (Freeman, 1958) were used for K and O. Anomalous scattering corrections were $+0{\cdot}2$ for K and $-1{\cdot}2$ for Re. Because K and Re are superimposed in the projection on (001), temperature factors for these atoms were obtained from the $(h0l)$ difference synthesis and were used in the $(hk0)$ difference synthesis. Successive approximations produced values of the parameters as follows:

$$\begin{array}{ll} B(\mathrm{Re}) = 0{\cdot}79 & x = 0{\cdot}131 \\ B(\mathrm{K}) = 3{\cdot}67 & y = 0{\cdot}041 \\ B(\mathrm{O}) = 2{\cdot}60 & z = 0{\cdot}210 \end{array}$$

The origin is taken at a symmetry center and the temperature factor is $\exp[-B(\sin^2\theta)/\lambda^2]$. Table 1 contains F_o and values of F_c calculated from these parameters. For only two unobserved reflections, (3,0,17) and (1,0,19), is F_c greater than the minimum detectable F_o. The R factor, $\Sigma|F_o-F_c|/\Sigma|F_o|$, is 5·6% for $(hk0)$ and 9·0% for $(h0l)$ reflections, only observed reflections being included in the summations. Because the metal atoms are in special positions, these small values are not wholly unexpected. On the other hand, it is of interest to note that inclusion of oxygen brings the R factors 3·5% below values obtained from metal atom scattering alone. Standard deviation for the location of oxygen atoms, calculated by the method of Cruickshank (1949), was 0·03 Å.

Discussion of the structure

Interatomic distances in $\mathrm{KReO_4}$ are:

Re–O	1·77 Å	O–O (same group)	2·80 Å 2·93
K–O	2·88 2·77	O–O (neighboring groups)	3·33 2·92
K–Re	4·02 4·26		

The O–Re–O angles in the $\mathrm{ReO_4^-}$ ion are 105° and 112°. The standard deviations are estimated to be 0·03 Å for the metal–oxygen separations and 0·06 Å for oxygen–oxygen separations. According to Cruickshank's (1949) criteria, differences in the oxygen–oxygen distances in the $\mathrm{ReO_4^-}$ ion as given above are only possibly significant; the same criteria indicate the difference in the potassium–oxygen separation to be significant. With these limitations in mind, one can describe the $\mathrm{ReO_4^-}$ ion as a tetrahedron distorted very slightly by elongation in the z direction, the four oxygens forming a tetragonal bisphenoid with corners equidistant from the central Re. The O–Re–O angles correspond closely to the value for a regular tetrahedron. All of the atomic separations listed above are equal to or greater than the sum of the van der Waals radii (Pauling, 1945). Since the smaller K–O distance (2·77 Å) is close to the radius sum (2·73 Å) and since the smallest O–O distance is equal to the radius sum (2·80 Å), the packing appears to be determined by both potassium–oxygen and oxygen–oxygen contacts. In this regard, $\mathrm{KReO_4}$ differs from $\mathrm{KIO_4}$ (Hylleraas, 1926) and $\mathrm{KRuO_4}$ (Silverman & Levy, 1954) where K–O separations are nearly the same and where K–O contacts determine the packing.

Comparison of the tabulated value of 0·52 Å for the Re^{+6} ionic radius with tabulated Mn ion radii (Wyckoff, 1948) leads to an estimate of 0·50 Å for Re^{+7}. The corresponding ionic Re–O distance is 1·90 Å, a value greater than the observed distance. This result is in accord with the suggestion (Pauling, 1945) that bonds in $M\mathrm{O_4^-}$ ions, where M is a heavy atom, probably have considerable double bond character.

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