by Ahrens (1952), but is in fairly good agreement with the values in Table 5 derived from the ionic distances W–O known in the $[WO_4]^{2-}$ ion of the structures AWO_4 ($A =$ Ba, Ca, Pb or Sr) given by Sillén & Nylander (1943).

Table 5 shows also the change of the ionic distances in the tetrahedral coordination with the radii, or with the polarization effect of the A cations. Also the NH_4^+ ion must have such an effect complicated to some extent by the protons around the N atom. The reduced ionic distance of W–O, as well as that of W–S can be attributed most probably to a partially covalent bond in the tetrahedron.

According to Fig. 4 and Table 4 the NH_4^+ ions have 9 and 10 nearest neighbours respectively, with distances ranging from 3·10 to 3·96 Å. The arrangement of the S^{2-} ions around NH_4^+ is rather irregular.

Although the structure of ammonium thiotungstate cannot be regarded as a close-packed one, a similarity to close packing can be detected. Parallel to the plane (100) corrugated ionic planes can be seen (broken lines show these planes for one period in Fig. 4), built up of S^{2-} and NH_4^+ ions and appearing with two different ionic arrangements given without distortion in Fig. 5. These two kinds of ionic plane A and B alternate in the crystal lattice according to the scheme ..$ABBABBA$... In Fig. 4 the period $BABB$ is given. The fitting of any two neighbouring ionic planes is pictured in Fig. 6(a), (b), (c) in which the distortion of the lattice is omitted. As the ionic planes are built up of S^{2-} anions and NH_4^+ cations in one (a, b) period of the unit cell, by fitting the AB and BA planes, only one tetrahedron and by fitting the BB planes, two tetrahedra are built with only S^{2-} ions at the

corners. Every other polyhedron of this ionic arrangement has at its corners different kinds of ions. If we put W atoms in the cavities surrounded only by S^{2-} ions and make a distortion by corrugating the related ionic planes which is necessary in order to separate from each other the atoms that are too near to one another in the undistorted arrangement, we come to the structure of ammonium thiotungstate.

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Order in Binary σ-Phases

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The atomic order in two σ-phase Re–Mo alloys has been determined using powder photographs and X-ray diffractometry. The proposed order schemes support the same correlation between the position of the element in the periodic table and the lattice site as that obeyed by σ-phases formed by elements of the first long period. Rhenium is similar to manganese in its ordering behaviour.

Introduction

The existence of the σ-phase in many binary and ternary alloys of the transition elements has been reported in recent years (Greenfield & Beck, 1956; Knapton, 1957; Nevitt & Downey, 1957) and the detailed structure of this phase has been carefully

determined for several representative alloys (Bergman & Shoemaker, 1954; Kasper, Decker & Belanger, 1952; Dickins, Douglas & Taylor, 1956). The existence of order in the σ-phase structure has been established in a number of alloys (Decker, Waterstrat & Kasper, 1954; Kasper & Waterstrat, 1956; Ageev & Shekhtman, 1959, 1960; Brown & Forsyth, 1961; Wilson &

Spooner, 1963). The aim of these investigations is to obtain information about the factors governing the structure of this phase.

The present X-ray investigation was carried out in order to determine the nature of the order present in the σ-phase formed by rhenium and molybdenum since there is a large difference in the atomic numbers of these two elements ($Z_{Re} - Z_{Mo} = 33$). The σ-phases were prepared by arc-melting in argon. The nominal compositions of the two alloys used were Re 55 at.%, Mo 45 at.% (ReMo55) and Re 68 at.%, Mo 32 at.% (ReMo68). According to Greenfield & Beck (1956)

Table 1. *X-ray data for* σ–WRe 50

hkl	Powder camera $\sin^2\theta \times 10^4$ Obs.	Calc.	Intensities Obs.	Calc.		Diffractometer intensities Obs.	Calc.	
110	—	128	—	<0·1		—	0·1	
200	—	256	—	<0·1		—	0·1	
101	—	300	—	4·8		—	4·7	
210	—	321	—	<0·1		—	0·1	
111	—	365	—	0·9		—	0·8	
220	—	513	—	<0·1		—	0·1	
211	—	557	—	0		—	0	
310	—	641	—	1·1		—	0·6	
221	—	749	—	3·9		—	1·7	
301	—	813	—	1·3		—	0·5	
320	—	834	—	0·7		—	0·3	
311	884	887	vw	41·8		18	16·2	
002	951	945	w	167		47	55·7	
400	—	1026	—	0·2		—	0·1	
321	—	1070	vvw*	4·6 } 26·1		233 }	1·5 } 231	
112	—	1073		21·5 }			6·6 }	
410	1098	1090	s	734		223 }		
330	1160	1154	m	358		101	103	
202	1207	1202	m	319		92	90	
212	1273	1266	s	679 } 681		183 }	180 } 181	
420		1282	—	2·2 }			0·6 }	
411	1334	1326	vs	1070		268	274	
331	1398	1390	s	534		129	129	
222	1464	1458	w	138		31	31·8	
421	—	1519	—	5·8		—	1·3	
312	1586	1586	w	174		36	36·7	
430	—	1603	—	0·8		—	0·2	
510	—	1667	—	4·7		—	1·0	
322	1786	1779	vw	43·9		9	8·5	
501	1842	1839	vw	3·2 } 50·1		10·4 }	0·6 } 9·4	
431		1859		46·9 }			8·8 }	
520	—	1859	—	<0·1		—	<0·1	
511	1909	1903	vw	46·7		8·1	8·5	
402	—	1971	—	6·4		—	1·1	
412	—	2035	—	4·8		—	0·8	
440	—	2052	—	0·1		—	0·2	
521	2098	2096	vvw	19·3 } 20·1		7 }	3·2 } 3·3	
332		2099		0·83 }			0·1 }	
530	—	2186	—	2·6		—	0·4	
103	—	2191	—	2·0		—	0·3	
422	—	2228	—	1·06		—	0·2	
113	—	2255	—	0·3		—	<0·1	
441	—	2288	—	0·2		—	<0·1	
600	—	2308	—	0·4		—	<0·1	
610	—	2372	—	<0·1		—	<0·1	
531	—	2416	—	<0·1		—	<0·1	
213	—	2447	—	<0·1		—	<0·1	
432	2553	2548	vw	59·8 } 65·6		11 }	8·74 } 9·6	
620		2565		5·8 }			0·83 }	
611	2617	2609	vw	1·2 } 66·5		10 }	0·17 } 9·3	
512		2612		65·3 }			9·17 }	
540	—	2629	—	4·9		—	0·7	
223	—	2640	—	1·9		—	0·2	
303	—	2704	—	0·6		—	0·1	
313	—	2768	vvw*	21·4		—	2·8	
621	2808	2801	w	29·6 } 169		19 }	3·75 } 21·4	
522		2805		139·6 }			17·64 }	

* Not measurable but visible. v = very; w = weak; m = medium; s = strong.

these σ-phases are stable above 1,200 °C and, accordingly, the melts were annealed at 2,000 °C before quenching. The alloys were extremely brittle and powder samples were prepared by crushing and grinding with an agate mortar.

In addition to the two rhenium-molybdenum alloys a sample of a σ-phase containing 50 at.% tungsten and 50 at.% rhenium (WRe50) was also submitted to X-ray examination. Since the difference in scattering factors of tungsten and rhenium is very small and the anomalous dispersion corrections for copper radiation are the same (Dauben & Templeton, 1955), this sample behaved as though it were disordered and thus served as a kind of standard for the detection of order in the rhenium-molybdenum alloys.

Experimental

Debye–Scherrer powder photographs of all the alloys were taken with a 19 cm precision camera using a copper target with nickel filter. Unit-cell sizes were obtained from the observations on high-angle lines using a Nelson–Riley extrapolation method. Line intensities were estimated visually up to $\sin^2 \theta = 0.4$. Beyond this limit the interference between α_1 and α_2 components of neighbouring lines made the estimation of line intensities difficult. Line intensities were calculated for various ordering schemes and for a random atom distribution in the unit cell using the atomic co-ordinates of σFe–Cr given by Bergman & Shoemaker (1954). Other investigations (Decker et al., 1954; Kasper & Waterstrat, 1956) have shown that these co-ordinates can be used with reasonable confidence with other σ-phases and their use should not introduce any serious error in intensity calculations for low hkl. The anomalous-dispersion corrections to scattering factors given by Dauben & Templeton (1955) have been included in all the calculations. An absorption correction for each alloy has been determined using the method described by Klug & Alexander (1954).

In order to obtain quantitative estimates of line intensities several runs were made with flat powder samples using a Hilger diffractometer with a stabilized Philips X-ray set and a curved quartz-crystal monochromator. Copper radiation was used with a xenon-filled proportional counter as detector connected to a single-channel pulse analyser set to received pulses from $K\alpha$ photons only. The diffraction pattern was recorded continuously at a chart speed of 3.75° of 2θ per hour.

The line intensities of the diffractometer specimens were determined by measuring the areas beneath peaks using a planimeter. These were compared with calculations based on the Bergman–Shoemaker parameters. The absorption factor was assumed constant over the range of 2θ measured (10° to 80° approx.). Preferred-orientation effects, which were troublesome with the WRe sample, were minimized by mixing the finely powdered sample with starch. The slight disagreement between observed and calculated intensities for 002 and 004 lines (Table 1) is attributed to this effect. The same procedure was adopted for the ReMo samples.

The diffractometer was set with an exit slit giving a horizontal divergence of 0.34°. With a time constant of five seconds and a thin sample of quartz powder which was used for calibration, the resolving power of the $20\bar{2}0$ line at 42° (approx.) was 3%. The use of Soller slits to improve the resolution was precluded because of the very small quantities of σ-phase samples available. Although reproducible results were obtained with the sample-starch mixtures, the intensities of medium and strong lines could not be estimated with an accuracy better than 10%; the weakest lines, which were most important in σ-phase order determination, could not be measured to better than 30 to 40%. The σ-phase is complex and the small intensity contributions from extremely weak lines, such as the unobserved lines of Table 1, give rise to a virtual background which makes the delineation of the 'wings' of measured lines somewhat uncertain. This effect, coupled with the asymmetry of line profiles, led to large uncertainties in very weak line intensities. The uncertainties in single runs were reduced by taking mean values from several runs.

Results

(i) σ-Phase WRe50

The unit-cell dimensions are

$$a = 9.6274 \pm 0.0005, \quad c = 5.0150 \pm 0.0005 \text{ Å},$$
$$c/a = 0.5209 .$$

This result is in good agreement with Greenfield & Beck (1956) who give $a = 9.55$, $c = 4.98$ Å, $c/a = 0.52$, for the WRe σ-phase. The values of $\sin^2 \theta$ and line intensities are given in Table 1. The good agreement between observed and calculated intensities, assuming a random distribution of atoms in the unit cell, gives some justification for using the Bergman & Shoemaker parameters.

(ii) σ-Phase ReMo55

The unit-cell dimensions are

$$a = 9.6010 \pm 0.0005, \quad c = 4.9850 \pm 0.0005 \text{ Å},$$
$$c/a = 0.5192 .$$

Previous investigators of this σ-phase quote: $a = 9.54$–9.58, $c = 4.95$–4.96 Å, $c/a = 0.52$ (Greenfield & Beck, 1956); $a = 9.54$, $c = 4.95$ Å, $c/a = 0.52$ for Re_3Mo_2 (Ageev & Shekhtman, 1959); $a = 9.588$, $c = 4.983$ Å, $c/a = 0.520$ for Re_3Mo_2 (Knapton, 1958).

Visual comparison of the WRe50 and ReMo55 Debye–Scherrer films shows only minor differences in the intensities of the two characteristic groups of strong σ-phase lines and on this evidence alone the

ReMo55 phase might be regarded as completely disordered. A comparison of overexposed films shows the following differences which are attributed to ordering:

From the composition of the alloy it is assumed than an average of 16·5 atoms of rhenium and 13·5 atoms of molybdenum are contained in the unit cell. The order scheme was determined by trial and error, guided by the requirements listed in Table 2. The relatively weak 002 line suggested that some Re atoms occupied E sites which have a negative structure amplitude. In order that 331 might be strong the D sites must be mainly occupied by Re atoms. Likewise, the observed intensity of 101 required

Table 2. Comparison of selected weak lines on ReMo55 and WRe50 films

hkl	$\sin^2 \theta$	Remarks
101	309	Much stronger on ReMo55 than WRe50
111	374	Seen on ReMo55 but not on WRe50
311	887	Much weaker on ReMo55 than WRe50
322	1786	This group of lines is relatively much stronger on ReMo55 than WRe50
131	1843	
511	1908	
402	1999	Easily seen on ReMo55 film but not on WRe50 film
432	2576	This pair of lines is appreciably weaker on ReMo55 than WRe50
611	2638	
512		

Table 3. Order scheme for ReMo55

Crystallographic site			Total no. of atoms	Site occupancy Re	Mo
A	(000)		2	2	Nil
B	(xx0)	(x = 0·3981)	4	1	3
C	(xy0)	(x = 0·4632) (y = 0·1316)	8	4	4
D	(xy0)	(x = 0·7376) (y = 0·0653)	8	6·5	1·5
E	(xxz)	(x = 0·1823) (z = 0·25)	8	3	5

Table 4. X-ray data for σ–ReMo 55

	Powder camera $\sin^2 \theta \times 10^4$		Intensities: calculated			Diffractometer Intensities: calculated		
hkl	Obs.	Calc.	Observed	Ordered	Random	Observed	Ordered	Random
110	—	129	—	—	—	—	<0·1	<0·1
200	—	258	—	0·3	—	—	0·3	<0·1
101	309	304	vvw	20·3	3·2	18	19·2	3·0
210	—	322	—	0·6	—	—	0·5	<0·1
111	374*	368	vvvw	4·1	0·6	4·6	3·4	0·5
220	—	516	—	0·9	—	—	0·5	<0·1
211	—	561	—	—	—	—	<0·1	0
310	—	645	—	0·6	0·8	—	0·3	0·4
221	—	755	—	1·3	2·8	—	0·5	1·1
301	—	819	—	—	0·9	—	<0·1	0·3
320	—	838	—	1·3	0·5	—	0·5	0·2
311	887	884	vvvw	16·1	30·1	5·8	5·4	10·1
002	952	957	mw	140	113	38	44·3	35·5
400	—	1032	—	1·3	0·4	—	0·4	0·1
321	—	1077	—	1·0	3·3	—	0·3	0·9
112 / 410	1093	1086 / 1096	vs	13 / 520 } 533	15·2 / 519 } 534	148 }	3·6 / 144 } 148	4·2 / 144 } 148
330	1157	1160	ms	257	256	70	65·6	65·2
202	1211	1214	m	218	227	57	55·1	57·4
212 / 420	1276	1279 / 1289	s	482 / 7·6 } 490	475 / 1·5 } 479	112 }	116 / 1·8 } 118	115 / 0·4 } 115
411	1332	1335	vvs	837	755	194	193	174
331	1397	1400	s	415	376	98	92·3	83·7
222	1467	1472	m–mw	97	91	23	20·8	19·6
421	1528*	1528	vvvw	3·1	4·0	—	0·6	0·8
312 / 430	1596	1601 / 1602	m	134 / 2·3 } 136	115 / 0·6 } 116	27 }	27·3 / 0·5 } 27·8	23·5 / 0·1 } 23·6
510	1680*	1676	—	6·3	3·2	—	1·2	0·6
322	1786	1795	w	49·1	28·8	10·4	9·2	5·4
501 / 431	1843	1851	w	4·5 / 50·7 } 55·2	2·1 / 31·2 } 33·3	10·6 }	0·8 / 9·3 } 10·1	0·4 / 5·7 } 6·1
520	—	1870	—	—	—	—	<0·1	<0·1
511	1908	1915	w	49·2	31·5	9·4	8·8	5·7
402	1999*	1988	vvvw	14·8	4·2	3·9	2·6	7·4
412 / 440	2062*	2052 / 2063	vvvw	12·7 / 0·2 } 12·9	3·2 / 0·2 } 3·4	3·5 }	2·1 / >0·1 } 2·1	0·5 / >0·1 } 0·5
521 / 332	2101	2109 / 2117	vvw	19·5 / 4·0 } 23·5	12·7 / 0·5 } 13·2	4·6 }	3·1 / 0·7 } 3·8	2·0 / 0·1 } 2·1
530	—	2192	—	0·3	1·7	—	<0·1	0·3
103	2222	2217	vvvw	8·3	1·3	—	1·3	0·2
422	—	2246	—	1·2	0·7	—	0·2	0·1

Table 4 (cont.)

hkl	Powder camera sin² θ × 10⁴		Intensities: calculated			Diffractometer Intensities: calculated		
	Obs.	Calc.	Observed	Ordered	Random	Observed	Ordered	Random
113	—	2281	—	1·8	0·3	—	0·3	<0·1
441	—	2302	—	1·0	0·1	—	0·2	<0·1
600	—	2321	—	—	0·3	—	0	<0·1
610	—	2385	—	0·7	—	—	0·1	<0·1
531	—	2431	—	—	—	—	<0·1	<0·1
213	—	2494	—	—	—	—	<0·1	<0·1
432	2576*	2568	vvvw	23·6 } 24·2	39·6 } 43·5	5·4 }	3·3 } 3·4	5·5 } 6·0
620		2579		0·6	3·9		0·1	0·5
611	2638*	2624	vvvw	1·1 } 26·4	2·3 } 45·5	5·2 }	0·1 } 3·5	0·3 } 6·1
512		2633		25·3	43·2		3·4	5·8
540	—	2643	—	0·3	3·1	—	<0·1	0·4
223	—	2668	—	0·6	2·6	—	0·1	0·2
303	—	2732	—	—	0·4	—	<0·1	<0·1
313		2797		7·2 }	13·9 }	}	0·9 }	1·8 }
621	2818	2818	vw	12·0 } 93·3	19·7 } 106	8·0 }	1·5 } 11·7	2·5 } 13·4
522		2826		74·1 }	72·4 }	}	9·3 }	9·1 }
541	2889*	2878	vvvw	6·6 } 7·3	13·8 }	—	0·8 } 0·9	1·7 } 1·7
630		2896		0·7		—	0·1	<0·1
323	—	2985	—	—	—	—	<0·1	0·1
442	—	3015	—	—	—	—	0·1	0·1
....								
631	3140	3135	m–ms	7·9 } 291	11·1 } 310	30·1 }	0·9 } 33	1·3 } 35·1
532		3143		283	298		32·1	33·8
550	3214	3218	w–mw	112 } 114	116 } 116		0·3	0·1
710				2·4	0·2		12·5	12·8
413	3242	3243	ms–s	417	377		47	42·4
602	3268	3272	m	154	162	124 }	17 } 115	17·9 } 109
333	3303	3307	m	218	198		23·7	21·5
612	3332	3336	m	137 } 137	134 } 135		14·5	14·2
640		3347		0·4	0·8		<0·1	<0·1
701	3407	3393	ms	25 } 303	24 } 320		2·5	2·4
720		3411		278	296		28·4	30·3
423	—	3436	—	5·5	3·6	45·5 }	0·6 } 50·8	0·4 } 49·5
711	3453	3457	m	1·1 } 190	0·3 } 162		0·1	<0·1
551				189	162		19·2	16·4
622	3527	3529	w	108	95	11·8	10·7	9·5
641	3590	3586	w	28 } 129	23 } 111	12·5 }	2·8 } 12·7	2·3 } 11·0
542		3594		101	88		9·9	8·7
721	3646	3650	ms	292	230	26·3	28·6	22·5
730	—	3733	—	0·8	0·2	—	0·1	0·1
503	3777*	3764	vvvw	2 } 27·6	0·7 } 20	—	0·2 } 2·6	0·1 } 1·9
433				25·6	19·3	—	2·4	1·8
004	3819	3820		222 } 256	213 } 235	16·9 }	20·1 } 23·1	19·2 } 21·1
513		3822	m	33·5	22		3·0	1·9

N.B. Values of sin² θ below dotted line refer to α₁ components.　　v = very;　w = weak;　m = medium;　s = strong.
　　* Indicates measurement made on overexposed film.

B sites to be filled mainly by molybdenum atoms and A sites filled by Re atoms. The refinement of an order scheme which satisfied the powder film data was obtained from a study of diffractometer intensities. The reliability of the final order scheme, which is given in Table 3, is such that a replacement of one atom of Re by Mo has an observable adverse effect. The calculated intensities for this scheme, normalized to the diffractometer intensities, and also for a random arrangement are given in Table 4; the powder film data are also given in this table.

(iii) σ-Phase ReMo68

The unit-cell dimensions are

$$a = 9\cdot5788 \pm 0\cdot0004, \quad c = 4\cdot9741 \pm 0\cdot0005 \text{ Å},$$
$$c/a = 0\cdot5193 .$$

This cell is slightly smaller than that of ReMo55, which supports the belief that Re atoms tend to occupy sites of smaller volume than those of Mo atoms.

Table 5. Order schemes for ReMo68

Site	Total no. atoms	Order scheme No. 1		Order scheme No. 2	
		Re	Mo	Re	Mo
A	2	2	Nil	2	Nil
B	4	2	2	1	3
C	8	4	4	4	4
D	8	8	Nil	8	Nil
E	8	4	4	5	3

Table 6. X-ray data for σ–ReMo 68

hkl	Powder camera $\sin^2\theta \times 10^4$ Obs.	Calc.	Intensities: calculated Obs.	Ord. 1	Ord. 2	Random	Diffractometer Intensities: calculated Obs.	Ord. 1	Ord. 2	Random
101	307	308	vvw	19·1	26·3	3·4	18·6	18·1	24·9	3·2
111	—	373	<vvw	5·5	7·1	0·6	4·3	4·6	5·9	0·5
311	896	895	<vvw	17·5	12·9	32·3	6·8	5·9	4·3	10·8
002	965	968	w	158	139	121	41·9	50	43·8	38·1
112, 410	1107	1096, 1109	s	11·2, 597·6 }609	16, 620 }636	572	169 }	3·4, 165 }169	} 176	} 157
330	1172	1174	m	278	293	274	81	70·9	75	70
202	1225	1226	mw	249	244	243	59·9	62·7	62	61·5
212, 420	1289	1291, 1304	ms	536, 10 }546	542, 11 }553	513	128 }	129·2, 2·2 }131	} 134	} 124
411	1348	1349	vs	922	881	809	209	213	203	187
331	1413	1414	ms	484	458	403	103	108	102	90
222	1483	1485	vw	117	126	98	26·5	25	26·9	21
421	1543	1544	<vvw	3·9	7·1	4·3	not obs.	0·8	1·5	0·9
312, 430	1614	1614, 1629	w	146, 3 }149	150, 5 }155	124	29·4 }	29·7, 0·6 }30·3	} 31·6	} 25·3
322	1807	1809	vw	48·5	64·3	30·9	10·7	9·1	12·1	5·8
501, 431	1865	1869	vw	4·1, 44·3 }48·4	6·6, 53·6 }60·2	35·7	10·2 }	0·7, 8·1 }8·8	} 11	} 6·5
511	1930	1934	vw	61	61	33·8	11·4	10·9	10·9	6·1
402	—	2004	vvw	14·7	19·9	4·5	2·8	2·6	3·5	7·9
412	—	2069	<vvw	13·1	6·2	3·4	2·5	2·1	1·0	0·5
521, 332	2122	2128, 2134	vvw	24, 2·4 }26·4	20·8, 1·5 }22·3	14·2	5·0 }	3·9, 0·4 }4·3	} 3·5	} 2·3
103	2235	2230	vvw	8·6	10·5	1·4	not obs.	1·4	1·7	0·2
432, 630	2586	2588, 2602	vvw	25·3, 1·4 }26·7	23·4, 1·9 }25·3	46·6	4·5 }	3·2, 0·3 }3·5	} 3·6	} 6·4
611, 512	2647	2647, 2653	vvw	<1, 38·2 }38·2	<1, 33·3 }33·3	48·8	4·3 }	<1, 5·1 }5·1	} 4·9	} 7·2
313	—	2806	not obs.	7·0	7·5	14·9		0·9 }		
621, 522	2843	2842, 2848	w	14·1, 74·3 }88·4	10·1, 79·3 }89·4	98·7	11·9 }	1·8, 9·5 }12·2	} 12·5	} 14·4
541	—	2907	not obs.	15	10·4	14·8	not obs.	1·9	1·3	1·8
631, 532	3166	3161, 3167	m	9·8, 308 }318	9·4, 322 }331	332	36·1	1·1, 35·1 }36·2	37·7	37·6

v = very; w = weak; m = medium; s = strong.

The powder photographs were a little spotty, making the visual estimation of lines more difficult than for ReMo55. The small differences in the results for the two alloys led to the two order schemes given in Table 5. For the purposes of ordering the unit cell was assumed to contain 20 Re atoms and 10 Mo atoms. The limited data given in Table 6, for low-angle lines only, do not warrant an unequivocal acceptance of either scheme but calculations on higher-angle lines favour scheme No. 1.

Discussion

The order schemes obtained by other workers for σ-phases are presented for comparison with the present results in Table 7. The σ-phase $Re_{18}Mo_{12}$ studied by Ageev & Shekhtman (1959) has a composition intermediate between those of the two Re–Mo alloys used in this work and the present results suggest the following ordering scheme for this alloy: A–2Re; B–1Re3Mo; C–4Re4Mo; D–7Re1Mo;

Table 7

	$Re_{18}Mo_{12}$[1]	$Re_{18}Cr_{12}$[2]	Re_2Cr[3]	Mn_3Cr[4]	$Mn_{19}Mo_{11}$[5]	$Re_{16·5}Mo_{13·5}$[6]	$Re_{20}Mo_{10}$[6]
Unit-cell size a	9·54 Å	—	9·290 Å	—	9·10 Å	9·601 Å	9·579 Å
c	4·95	—	4·831	—	4·74	4·985	4·974
c/a	0·52	—	0·52	—	0·52	0·519	0·519
Site A	Re	Re	Assumed	Mn	Mn	Re	Re
B	Mo	Cr	Disordered	3Mn, 1Cr	Mo	1Re, 3Mo	2Re, 2Mo
C	Re	Re		5Mn, 3Cr	5Mn, 3Mo	4Re, 4Mo	4Re, 4Mo
D	Re	Re		Mn	Mn	6·5Re, 1·5Mo	Re
E	Mo	Cr		4·5Mn, 3·5Cr	4Mn, 4Mo	3Re, 5Mo	4Re, 4Mo

[1] Ageev & Shekhtman, 1959.   [2] Ageev & Shekhtman, 1960.   [3] Waterstrat & Kasper, 1957.
[4] Kasper & Waterstrat, 1956.   [5] Decker et al., 1954.   [6] Present results.

E–4Re4Mo. This shows agreement with Ageev & Shekhtman for A, B and D sites only, and further-more, Ageev & Shekhtman reject an order scheme with C and E sites filled in the manner suggested. Unfortunately, no comparable details of line inten-sities are given in their paper.

It is interesting to compare the present order schemes for σRe–Mo with those of σMn–Cr and σMn–Mo, since manganese and rhenium on the one hand and Mo and Cr on the other belong to the same group in the periodic table. The order schemes for σMn–Cr and σMn–Mo are almost alike with Cr and Mo playing the same role and the excess Mn atoms in Mn_3Cr tending to fill up B sites rather than C and E sites. The proposed schemes for ReMo55 and ReMo68 are very similar, with Re behaving like Mn and Mo behaving like Cr, except in the filling of B sites. It follows from this comparison that the chemical factor associated with the positions of the alloying elements in the periodic table is an important one in deciding the nature of the order in σ-phases. In contrast to this, it has been noted by Greenfield & Beck (1956) that the mean compositions of the σ-phases formed by rhenium correspond closely to that of σMn–Mo but not σMn–Cr.

Assuming Re behaves like Mn, σRe–Cr should be ordered like σMn–Cr and σRe–Mo, but the results given in Table 7 are conflicting on this point. Ageev & Shekhtman give the same order scheme for σReCr as σReMo, whilst Waterstrat & Kasper (1957) state that their σReCr is disordered. A more detailed analysis of this phase is required because the Ageev & Shekhtman scheme is based on six strong lines only and the Waterstrat & Kasper scheme is derived from a 5 cm powder film. As noted above, the main evidence for order is obtained from a detailed study of weak lines.

For σ-phases formed between metals of the first long period and also with molybdenum, a correlation between the position of the element to the left (X) or to the right (Y) of manganese in the periodic table, the co-ordination number and effective volume of site occupied in the ordered structure has been noted by Kasper & Waterstrat (1956) as follows:

Site	Co-ordination No.	Volume of site	Occupancy
A	12	Small	Y
B	15	Large	X
C	14	Medium	Mixed
D	12	Small	Y
E	14	Medium	Mixed

This correlation is maintained approximately by the σ-phase discussed above formed by rhenium from the third long period and molybdenum from the

second long period, with rhenium behaving like Y. In σReFe the same correlation is observed with Re behaving like X (Ageev & Shekhtman, 1960) and this dual role is similar to that of manganese itself, which also behaves like X and Y (Kasper & Waterstrat, 1956).

Further correlations have been sought between alloying elements in σ-phases and observed order and, in particular, it has been noted that the volume associated with the crystallographic sites is in ac-cordance with the size of the atomic radii of the elements. This is not applicable to Re and Mo which have very similar radii: $r_{Re} = 1.37$ and $r_{Mo} = 1.38$ Å, and the main conclusion which can be drawn from the present work is that rhenium acts like manganese in its ordering behaviour in σ-phases.

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