

Fig. 5. Transmission factor *versus* r/R for case $\mu_2 = 0$, $2\theta = 90^\circ$.

Graphs like those in Figs. 4 and 5 allow optimum dimensions to be chosen for the target, from the standpoint of the transmission factor in diffraction studies. They also allow the value of the transmission factor to be found for non-tabulated α and β values, by an interpolation method.

Fig. 6 shows a plot of the transmission factor *versus* scattering angle for $\alpha = 0.4$ and for various values of the parameter β . The smallness of its variation with the scattering angle makes it easy to find, by interpolation, the values of the transmission factor for other scattering angles.

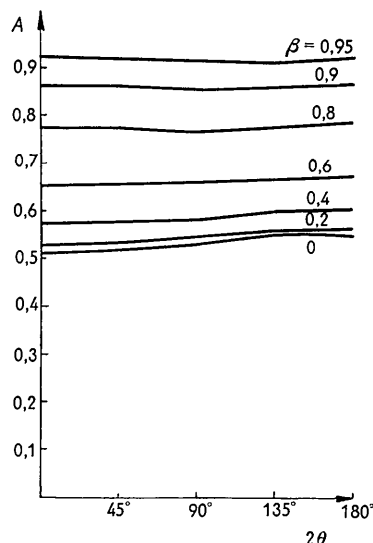


Fig. 6. Transmission factor *versus* scattering angle for case $\mu_2 = 0$, $\mu_1 R = 0.4$.

We wish to express our gratitude to G. Alămoreanu, D. Bădescu, M. Suveică, for assistance given in tabulating the transmission factor.

References

- BRADLEY, A. J. (1935). *Proc. Phys. Soc. Lond.* **47**, 879.
 CLAASSEN, A. (1930). *Phil. Mag.* **9**, 57.
International Tables for X-ray Crystallography (1959).
 Vol. II, p. 295. Birmingham: Kynoch Press.
 MØLLER, E. & JENSEN, E. (1952). *Acta Cryst.* **5**, 345.

Acta Cryst. (1964). **17**, 1533

Ordering in Binary σ Phases

BY F. J. SPOONER AND C. G. WILSON

Royal Military College of Science, Shrivenham, Swindon, Wiltshire, England

(Received 25 November 1963)

An X-ray diffraction study has been made of the ordering of atoms in the following binary σ phases: NbOs, NbIr, NbRe, MoOs, MoIr and CrRe. Ordering of atoms among the different atomic sites has been shown to exist in all cases. From these results and others it is deduced that the size of the constituent atoms is a major factor in governing the filling of A , B , and D sites but in addition some valency electron factor governs the filling of C and E sites.

Introduction

Considerable work has been done in recent years on binary σ phases involving transition metals of all three long periods. Comprehensive surveys on the stability and composition of these phases have been carried out by Knapton (1958) and Greenfield & Beck (1956), but most of this work has been confined to

phases involving elements in the first and second long periods. This report is concerned with an X-ray diffraction investigation of the order involved in additional σ phases consisting of elements of the second and third long periods: NbOs, NbIr, NbRe, MoOs, MoIr, WOs and in addition, a σ phase of particular interest: CrRe.

Table 1. Intensity data for σ phases

σ phase:	Nb ₃ Os ₂			Nb ₃ Ir ₂			Mo _{19.5} Os _{10.5}			Mo _{21.5} Ir _{8.5}			Cr ₂ Re ₃			Nb _{13.5} Re _{16.5}			WO ₂							
	a (Å)	c (Å)	c/a	I_0	I_c	I_r	I_0	I_c	I_r	I_0	I_c	I_r	I_0	I_c	I_r	I_0	I_c	I_r	I_0	I_c	I_r	I_0	I_c	I_r		
110	122	6	7	—	—	—	128	—	3	—	2	128	—	—	124	—	—	—	—	—	128	—	—	—		
200	245	—	—	—	—	—	256	—	—	—	1	256	—	—	248	—	—	—	—	—	256	—	—	—		
101	293	86	81	5	—	—	307	45	50	4	52	305	50	52	5	321	4	3	7	291	64	67	5	303	4	3
210	306	6	2	—	—	—	321	9	4	—	4	320	7	4	—	343	—	2	—	—	310	—	—	—	320	—
111	354	26	23	2	—	—	371	13	15	1	17	369	19	17	1	390	—	2	2	353	14	14	1	367	—	1
220	489	—	—	—	—	—	513	4	5	—	6	512	4	6	—	549	—	—	—	496	4	3	—	512	—	—
211	538	6	6	—	—	—	564	4	5	—	9	561	6	9	—	596	—	2	—	539	—	—	—	559	—	—
310	612	—	—	1	—	—	642	—	1	1	—	640	—	—	1	686	2	4	—	620	—	1	1	640	—	—
221	721	—	—	2	—	—	756	—	2	1	2	753	4	3	2	801	—	2	2	725	—	—	2	751	—	1
301	782	8	12	—	—	—	821	8	5	—	5	817	6	5	—	870	13	9	—	806	—	—	—	815	—	—
320	795	—	—	—	—	—	834	—	—	—	—	831	—	—	—	892	—	—	—	806	—	3	—	832	—	—
311	843	—	—	20	—	—	885	—	1	15	—	881	—	2	18	939	41	39	24	849	—	3	20	879	8	12
002	927	78	76	69	—	—	931	64	78	61	62	966	67	70	62	1011	82	81	84	914	72	78	70	956	37	43
400	978	5	6	—	—	—	976	6	5	—	3	1023*	45	3	—	1098	3	3	—	992*	18	3	—	1024*	30	—
321	1027	—	—	2	—	—	1026	—	—	1	—	1073	—	—	2	1145	—	—	—	1035	—	—	—	1071	—	1
112	1050	236	254	282	—	—	1053	187	209	252	—	1100	—	—	—	1148	343	361	339	1038	234	259	280	1084	174	173
410	1040	—	—	—	—	—	1038	—	—	—	—	1091	—	—	—	1166	—	—	—	1054	—	—	—	1089	—	—
330	1101	87	99	124	—	—	1099	92	82	111	—	1151	95	86	112	1235	140	141	148	1116*	206	109	123	1153	96	77
202	1172	72	79	114	—	—	1175	62	65	101	—	1229	57	59	85	1285	139	141	138	1162*	250	90	114	1212	71	70
212	1233	216	196	211	—	—	1236	176	157	188	—	1293	—	—	—	1354	290	274	259	1224	182	183	213	1276	154	131
420	1233	—	—	—	—	—	1231	—	—	—	—	1284	—	—	—	1372	—	—	—	1240	—	5	—	1281	—	—
411	1271	323	305	331	—	—	1270	270	281	295	—	1334	240	249	255	1419	407	391	400	1283	300	315	326	1328*	354	205
331	1333	183	167	159	—	—	1331	151	150	141	—	1398	148	134	120	1488	198	193	189	1345	170	158	157	1392	101	98
222	1417	35	43	38	—	—	1419	30	36	34	—	1485	26	34	28	1560	49	48	45	1410	42	42	38	1468	21	24
421	1455	—	—	—	—	—	1453	—	1	1	—	1527	—	1	1	1625	—	2	1	1469*	15	3	1	1520	—	1
312	1539	46	53	43	—	—	1541	38	44	39	—	1614	37	37	32	1697	29	39	52	1534	52	51	43	1597	25	27
430	1529	—	—	—	—	—	1526	—	—	—	—	1604	—	—	—	1715	—	—	—	1550	—	2	—	1601	—	—
510	1590	—	—	—	—	—	1587	6	2	1	—	1669	—	1	1	1784	—	—	—	1612*	45	4	1	1665	—	1
322	1722	21	22	10	—	—	1724	22	19	9	—	1806	18	16	8	1903	4	7	12	1720	23	23	10	1789	6	6
501	1761	24	18	10	—	—	1758	20	17	9	—	1847	18	13	8	1968	8	7	12	1779	23	18	10	1840	5	6
431	1761	—	—	—	—	—	1758	—	—	—	—	1847	—	—	—	1968	—	—	—	1779	—	—	—	1840	—	—
520	1773	—	—	—	—	—	1770	—	1	—	—	1861	—	1	—	1989	—	—	—	1798	—	—	—	1857	—	—

511	1822	28	27	10	1819	26	23	9	1912	21	19	8	1904	19	22	9	2036	5	7	12	1841	26	19	10	1904	5	6
402	1906	9	7	—	1907	8	6	—	1999	5	4	—	1989	—	4	—	2109	—	—	—	1907	8	5	—	1981	—	—
412	1967	6	5	1	1968	10	8	1	2063	7	5	1	2053	8	5	1	2177	—	—	—	1969	—	3	—	2045	—	—
440	1957	11	9	4	1953	8	8	4	2054	—	—	—	2047	6	6	4	2195	—	—	—	1984	—	—	—	2049	—	—
521	2005	—	—	—	2003	—	—	—	2104	8	5	3	2096	—	—	—	2242	—	2	5	2027	7	6	4	2096	3	3
332	2028	—	—	—	2029	—	—	—	2127	—	—	—	2117	—	—	—	2246	—	—	—	2031	—	—	—	2109	—	—
530	2079	—	—	—	2075	—	—	—	2182	—	—	—	2175	—	—	—	2332	—	—	—	2109	4	5	—	2177	—	—
103	2148	12	11	—	2155	8	10	—	2251	6	6	—	2237	12	6	—	2343	—	—	—	2109	—	—	—	2177	—	—
422	2150	—	—	—	2151	—	—	—	2256	—	—	—	2245	—	—	—	2383	2	4	—	2155	—	1	—	2237	—	—
113	2209	—	1	—	2216	—	1	—	2315	—	1	—	2301	—	1	—	2412	—	—	—	2181	—	—	—	2237	—	—
441	2189	—	1	—	2186	—	1	—	2297	—	—	—	2288	—	1	—	2448	—	—	—	2213	—	—	—	2288	—	—
600	2201	—	—	—	2197	—	—	—	2310	—	—	—	2303	—	—	—	2470	—	—	—	2233	—	—	—	2305	—	—
610	2263	—	—	—	2258	—	—	—	2375	—	—	—	2367	—	—	—	2538	—	—	—	2295	—	—	—	2369	—	—
531	2311	—	—	—	2308	—	—	—	2425	—	—	—	2416	—	—	—	2585	—	—	—	2337*	28	—	—	2416	—	—
213	2392	—	—	—	2399	—	—	—	2508	—	1	—	2493	—	1	—	2618	—	—	—	2367	—	—	—	2472	—	—
432	2456	—	2	11	2456	—	1	9	2577	—	1	8	2566	—	2	9	2726	—	—	—	2465	—	3	10	2557	—	—
620	2446	—	—	—	2441	—	—	—	2567	—	—	1	2558	—	—	—	2744	—	21	20	13	—	—	1	2561	—	—
611	2495	—	—	—	2491	—	—	—	2618	—	—	—	2608	—	—	—	2791	—	22	19	12	—	—	—	2608	—	—
512	2517	—	8	11	2517	—	4	9	2641	3	5	8	2629	4	7	10	2795	—	—	—	2523	—	4	11	2608	—	—
540	2507	—	—	—	2502	—	—	—	2631	—	—	1	2622	—	—	—	2813	—	—	2	1	—	—	—	2621	—	—
223	2576	—	1	—	2582	—	—	—	2701	—	—	—	2685	—	1	—	2823	—	—	—	2543	—	—	—	2625	—	—
303	2637	—	1	—	2643	—	—	—	2765	—	—	—	2749	—	—	—	2892	—	—	—	2553	—	—	—	2664	—	—
313	2698	—	1	3	2704	—	—	3	2829	—	—	2	2821	—	1	3	2961	—	—	—	2615	—	—	—	2728	—	—
621	2678	—	1	5	2674	—	—	1	2810	—	—	4	2800	—	4	—	2997	—	—	—	2677	—	—	2	2792	—	—
522	2700	8	7	21	2700	10	7	19	2833	6	7	17	2813	8	8	21	3000	—	35	40	30	—	—	—	2800	—	—
541	2739	—	2	4	2735	—	—	1	2874	—	1	3	2864	—	3	4	3065	—	—	—	2709	11	14	26	2813	11	14
630	2752	—	2	—	2746	—	—	1	2888	—	1	—	2878	—	1	—	3087	—	6	8	4	—	—	—	2864	2	3
323	2881	—	—	—	2887	—	—	—	3022	—	—	—	3013	—	—	—	3166	—	—	—	2791	—	—	—	2881	—	—
442	2884	—	—	—	2884	—	—	—	3026	—	—	—	3005	—	—	—	3206	—	—	—	2863	—	—	—	2984	—	—
631	2984	—	1	2	2979	—	1	2	3131	—	1	2	3120	—	—	—	3340	—	—	—	2899	—	—	—	3005	—	—
532	3006	47	44	61	3006	42	40	55	3154	30	31	50	3140	47	42	61	3343	—	80	78	97	—	—	—	3120	—	—
710	3058	—	20	23	3052	—	27	19	3209	—	—	—	3198	—	—	—	3430	—	—	—	3019	60	49	62	3133	36	41
550	3058	—	—	—	3052	—	—	—	3209	19	16	19	3198	23	18	22	3430	—	—	—	3023	—	—	—	3133	—	—
413	3126	100	103	108	3131	97	100	96	3278	73	87	89	3260	90	99	104	3441	—	250	234	257	—	—	—	3240	65	73
602	3128	—	—	—	3128	—	—	—	3283	—	—	—	3268	—	—	—	3481	—	—	—	3111	110	92	108	3261	—	—
333	3187	54	63	63	3192	57	62	57	3342	48	54	53	3324	61	62	62	3509	—	—	—	3147	80	29	32	3261	—	—
612	3190	—	—	—	3189	—	—	—	3348	—	—	—	3332	—	—	—	3549	—	—	—	3209	33	26	25	3325	—	—
R		0-090	0-275			0-097	0-281			0-087	0-243		0-117	0-240		0-056	0-087		0-079	0-222							0-109

I_o : Observed intensities. I_c : Calculated intensities (ordered). I_r : Calculated intensities (random).

* Lines coincident with impurity phase.

Experimental

The preliminary work was done with X-ray powder photographs obtained with a 19 cm Debye-Scherrer camera and Ni-filtered Cu $K\alpha$ radiation, the theoretical intensities being compared with those observed visually. More accurate results were obtained with an X-ray diffractometer and Cu $K\alpha$ radiation obtained from a stabilized X-ray set and monochromatized by a bent quartz crystal. A proportional counter with single-channel pulse discrimination was used for detection and relative line intensities were obtained by measuring areas beneath the peaks on the recorder traces.

The presence of order was detected by the comparison of observed (diffractometer) and calculated line intensities. The detailed nature of the order was obtained by the method of trial and error, the final order scheme adopted being that which gave the best agreement between observed and calculated intensities. This method was very suitable because of the appreciable difference in scattering factors between the constituents of the σ phases chosen for the investigation (except σ -WOs). All calculated intensities were corrected for anomalous dispersion by means of the data given by Dauben & Templeton (1955). The atomic parameters used for these calculations are those determined by Bergman & Shoemaker (1954) for σ -FeCr. Since the results obtained are based mainly on low-angle lines, small inaccuracies in atomic parameters will have little effect on the results. The σ -WOs powder film provided an excellent reference film for the detection of order in other σ phases because of its similar cell size and the apparent

random order displayed by virtue of the similarity of W and Os scattering factors. The agreement between observed and calculated intensities based on random order for this phase gives support for the wider use of the Bergman & Shoemaker parameters.

During the course of the investigation unit-cell sizes were determined from the Debye-Scherrer photographs with the use of the Nelson-Riley extrapolation method wherever possible; these measurements, together with the relevant intensity data for each sample, are given in Table 1. The order schemes used for the calculated intensities given in this table are included in the data given in Table 2. The normalization scheme chosen for the comparison of observed and calculated intensities was the summation of all intensity values excluding those which were associated with an impurity phase. A reliability index, $R = \Sigma(I_c - I_o) / \Sigma I_o$, was calculated for each σ phase, for both ordered and random schemes, again ignoring impurity lines, and is quoted in Table 1.

The final order schemes for CrRe and NbRe are excellent, the slightly higher value of R for NbRe being caused by the presence of the χ phase previously noted by Knapp. The σ phases NbOs, NbIr, MoOs, and MoIr have caused some difficulty owing to the appearance of the 210 reflexion which is very sensitive to order. It proved impossible to give this reflexion a higher calculated intensity consistent with a low value of R .

Some indication of the criterion for choosing a particular order scheme can be seen by examining the results in more detail, for example, the chosen order scheme for σ -MoIr having Ir atoms in 1A, 6-5D and 1E has a value for R of 0.117. The transfer of

Table 2. Ordering schemes for σ phases

r_x	σ phase		r_y	Composition		Site A		Site B		Site C		Site D		Site E		Valency electrons per atom	Reference
	X	Y		At.% X	At.% Y	X	Y	X	Y	X	Y	X	Y	X	Y		
(1.36)	V	Ni	(1.24)	69	31	0.3	1.7	3.9	0.1	7.5	0.5	1.1	6.9	7.9	0.1	6.4	(a)
(1.36)	V	Ni	(1.24)	64	36	0.2	1.8	4	0	6.5	1.5	0.7	7.3	7.9	0.1	6.8	(a)
(1.36)	V	Ni	(1.24)	61	39	0.3	1.7	4	0	5.6	2.4	1.0	7.0	7.5	0.5	7.1	(a)
(1.36)	V	Fe	(1.27)	60	40	0.3	1.7	4	0	6.5	1.5	1.2	6.8	6	2	6.2	(a)
(1.28)	Cr	Mn	(1.31)	25	75	0	2	1	3	3	5	0	8	3.5	4.5	6.75	(a)
(1.28)	Cr	Co	(1.26)	53	47	0	2	4	0	8	0	0	8	4	4	7.4	(b)
(1.28)	Cr	Fe	(1.27)	40	60	0	2	4	0	0	8	0	8	8	0	7.2	(c)
(1.40)	Mo	Fe	(1.27)	50	50	0	2	3	1	6	2	0	8	6	2	7.0	(d)
(1.40)	Mo	Mn	(1.31)	37	63	0	2	4	0	3	5	0	8	4	4	6.63	(e)
(1.40)	Mo	Co	(1.26)	60	40	0	2	4	0	7	1	0	8	7	1	7.2	(f)
(1.40)	Mo	Re	(1.37)	33	67	0	2	2	2	4	4	0	8	4	4	6.67	(g)
(1.40)	Mo	Re	(1.37)	45	55	0	2	3	1	4	4	1.5	6.5	5	3	6.55	(g)
(1.47)	Nb	Os	(1.34)	60	40	0	2	4	0	8	0	0	8	6	2	6.2	(h)
(1.47)	Nb	Ir	(1.35)	60	40	0	2	4	0	7	1	0	8	7	1	6.6	(h)
(1.47)	Nb	Re	(1.37)	45	55	0	2	4	0	4.75	3.25	0	8	4.75	3.25	6.1	(h)
(1.40)	Mo	Os	(1.34)	65	35	0.5	1.5	4	0	7.5	0.5	0.5	7.5	7	1	6.7	(h)
(1.40)	Mo	Ir	(1.35)	72	28	1	1	4	0	8	0	1.5	6.5	7	1	6.85	(h)
(1.28)	Cr	Re	(1.37)	40	60	1.5	0.5	1	3	2.5	5.5	4	4	3	5	6.6	(h)

(a) Kasper & Waterstrat (1956)

(b) Dickins, Douglas & Taylor (1956)

(c) Bergman & Shoemaker (1954)

(d) Wilson & Spooner (1963)

(e) Decker, Waterstrat & Kasper (1954)

(f) Forsyth & d'Alte da Veiga (1963)

(g) Wilson (1963)

(h) Present work

one Ir atom from a *D* site to an *A*, *B* or *C* site results in values of *R* of 0.144, 0.101 and 0.110, respectively, and transfer of one atom from an *E* site to an *A*, *B* or *C* site results in values of *R* of 0.175, 0.144 and 0.120, respectively. These results suggest that the transfer of an Ir atom from a *D* site to a *B* site was desirable, but although the intensity agreement among the stronger reflexions is improved, the agreement among the low-angle lines is extremely poor. The adopted order schemes are those which gave as low a value of *R* as possible consistent with the requirement for good agreement with low angle lines and missing reflexions. As Wilson (1963) has pointed out for other σ phases, the presence of order is indicated by the missing and weak line intensities.

The validity of the chosen order schemes is also indicated to some extent by comparing the values of *R* with that for WOs, which is 0.109. Since this phase can be assumed to have random order because of the similarity in scattering factors for the constituent elements, there can be no improvement in the value of *R*.

Discussion

Order schemes which have been determined experimentally for various σ phases are given in Table 2. The elements constituting each σ phase are characterised as X or Y, where X denotes an element to the left of manganese in the periodic table and Y an element to the right of manganese. Manganese and rhenium, which belong to the same group in the periodic table, are represented as Y-type elements. The Goldschmidt radius for coordination number 12 is given (in Å) in brackets at the side of each element.

It was pointed out by Kasper & Waterstrat in 1954, that atoms of type Y generally occupy sites *A* and *D* which have the smallest coordination number (12) and smallest volume, atoms of type X generally occupy the site *B* which has the largest coordination number (15) and the largest volume, and sites *C* and *E*, which have the intermediate coordination number (14) and intermediate volume may be occupied by a mixture of X and Y atoms. This generalization applies to the order schemes proposed for the σ phases NbRe, NbOs, NbIr, MoOs and MoIr but not for σ -CrRe. The generalization suggests the importance of the chemical nature of the constituent atoms in σ -phase order, but because of the characteristic variation of atomic size associated with the transition elements of each long period, the importance of the size effect in ordering becomes very apparent. The total number of valency electrons in *s* and *d* shells of the binary constituents (n_e) is also important in controlling order in some crystallographic sites as indicated below. For the σ phases listed in Table 2 the nature of the ordering associated with each crystallographic site may be summarized as follows:

Site A (0, 0, 0) (CN 12): Occupied mainly by Y atoms except for σ -MoIr and σ -CrRe; $r_x > r_y$ except for σ -CrRe and σ -CrMn; independent of n_e .

Site B ($x, x, 0$; $x=0.3981$) (CN 15): Occupied mainly by X atoms except for σ -CrMn, σ -CrRe and σ -MoRe; $r_x < r_y$ for σ -CrMn and σ -CrRe.

Site C ($x, y, 0$; $x=0.4632, y=0.1316$) (CN 14): Occupied by X and Y atoms but X atoms predominate except when Y=Mn or Re; domination by X increases with n_e ; site equally divided when Y=Mn or Re.

Site D ($x, y, 0$; $x=0.7376, y=0.0653$) (CN 12): Occupied mainly by Y atoms; $r_x > r_y$ except for σ -CrRe and σ -CrMn.

Site E (x, x, z ; $x=0.1823, z=0.2524$) (CN 14): Occupied by X and Y atoms; Y atoms predominate for large n_e .

The fact that *A* and *D* sites are usually filled by Y atoms having smaller radii suggests the ordering requirements of size and chemical nature. Similar factors govern the filling of the large *B* sites. In particular, when the larger atom is Y-type as happens in σ -CrMn and σ -CrRe, the majority of *B* sites are filled by Y atoms. The size factor is not apparent in filling up the intermediate *C* and *E* sites, except for large values of n_e . The phases containing Mn or Re are always distinguished by the mixed nature of the filling in *C* and *E* sites. A more detailed comparison of the exceptional phases CrMn, MoMn, MoRe and CrRe in which X and Y come from groups VI and VII of the periodic table shows that they have marked similarity in their ordering schemes. This aspect is much less apparent for σ phases whose atoms come from different groups of the periodic table.

The effect of an increasing valency electron contribution *per atom* can be estimated by considering the following series of σ phases:

1. NbRe(6.1), VFe(6.2), NbOs(6.2), NbIr(6.6), VNi(7.1).
2. MoRe(6.55), CrMn(6.75), MoIr(6.85), MoFe(7.0), MoCo(7.2).

In series 1 the X atom has five valency electrons and in series 2 it has six valency electrons, the average number of valency electrons per atom, of the unit cell being given in brackets. As the number of valency electrons per atom increases in each series the order approaches the simplest form in which Y atoms fill *A* and *D* sites only and X atoms fill *B*, *C* and *E* sites only.

The above results suggest that complex systematics, taking into account the size effect, the electronic factor and the chemical factor, govern the ordering in σ phases. The stability of the phase and its composition range would also seem to depend upon satisfying the ordering requirements since the only

σ phases reported as being randomly ordered are σ -CrOs, σ -CrRe and σ -CrRu (Waterstrat & Kasper, 1957). The latter authors suggested random ordering for σ -CrRe but the results given above disprove this. So far the stability of the phase has been variously attributed to electronic effects (Sully, 1951; Bloom & Grant, 1953; Greenfield & Beck, 1954) and close-packing of spheres (Frank & Kasper, 1958; Stüwe, 1959). On the other hand, Haworth (1960) concludes that the occurrence of the σ phase cannot be predicted from normal intermediate phase considerations.

If the ordering requirements are an essential feature of this phase the random ordering reported in σ -CrOs and σ -CrRu requires an explanation. Since $r_{Cr} = 1.28 \text{ \AA}$ and $r_{Os} = 1.34 \text{ \AA}$ the Y atom Os is larger than the X atom Cr, so that the normal requirements (smaller atom and type Y) for filling *A* and *D* sites cannot be satisfied and in this respect the phase is similar to σ -CrRe examined above. Following the latter example, *B* sites would be filled by Y and X atoms, and, since the number of valency electrons per atom is only 6.6 for the composition used (OsCr₂), it is expected that *C* and *E* sites would have mixed occupants. Thus, the presence of order might be difficult to detect and, in fact, Waterstrat & Kasper state that their measurements were not accurate enough to detect small amounts of ordering. Exactly similar arguments apply to σ -CrRu since Ru and Os belong to the same group of the periodic table.

From such considerations the general requirements for the stability of the σ phase formed by transition elements appear to be (i) a favourable atom size ratio ($r_x/r_y = 0.9-1.1$ in Table 2), (ii) the number of valency electrons per atom must lie within definite limits (6.1-7.4 in Table 2), and (iii) the elements X and Y must belong to the appropriate groups of the periodic table as defined above. These requirements are not satisfied when one of the binary elements is a non-transition element as in σ -Nb₂Al (Forsyth, 1961) and σ -ZrRe (Tylkina, Povarova &

Savitskii, 1960) and other factors are required to explain the occurrence of the σ phase in these systems.

The authors wish to thank Dr A. G. Knapton for providing the σ -phase specimens, Mrs M. Parselle for assistance with the diffractometer measurements and Dr J. Adam for much valued advice. This work was greatly assisted by the provisions of an extramural contract with the U.K.A.E.A. Harwell.

References

- BERGMAN, G. & SHOEMAKER, D. P. (1954). *Acta Cryst.* **7**, 857.
 BLOOM, D. S. & GRANT, N. J. (1953). *Trans. Amer. Inst. Min. (metall) Engrs.* **197**, 88.
 DAUBEN, C. H. & TEMPLETON, D. H. (1955). *Acta Cryst.* **8**, 841.
 DECKER, B. F., WATERSTRAT, R. M. & KASPER, J. S. (1954). *Trans. Amer. Inst. Min. (metall) Engrs.* **200**, 1406.
 DICKINS, G. J., DOUGLAS, A. M. B. & TAYLOR, W. H. (1956). *Acta Cryst.* **9**, 297.
 FORSYTH, J. B. (1961). *Acta Cryst.* **14**, 362.
 FORSYTH, J. B. & D'ALTE DA VEIGA, L. M. (1963). *Acta Cryst.* **16**, 509.
 FRANK, F. C. & KASPER, J. S. (1958). *Acta Cryst.* **11**, 184.
 GREENFIELD, P. & BECK, P. A. (1954). *Trans. Amer. Inst. Min. (metall) Engrs.* **200**, 253.
 GREENFIELD, P. & BECK, P. A. (1956). *Trans. Amer. Inst. Min. (metall) Engrs.* **206**, 265.
 HAWORTH, C. W. (1960). *J. Less Common Metals*, **2**, 125.
 KASPER, J. S. & WATERSTRAT, R. M. (1956). *Acta Cryst.* **9**, 289.
 KNAPTON, A. G. (1958). *J. Inst. Metals*, **87**, 28.
 STÜWE, H. P. (1959). *Trans. Amer. Inst. Min. (metall) Engrs.* **215**, 408.
 SULLY, A. H. (1951-52). *J. Inst. Metals*, **80**, 173.
 TYLKINA, M. A., POVAROVA, K. B. & SAVITSKII, E. M. (1960). *Dokl. Akad. Nauk SSSR*, **131**, 332.
 WATERSTRAT, R. M. & KASPER, J. S. (1957). *Trans. Amer. Inst. Min. (metall) Engrs.* **209**, 872.
 WILSON, C. G. (1963). *Acta Cryst.* **16**, 724.
 WILSON, C. G. & SPOONER, F. J. (1963). *Acta Cryst.* **16**, 230.