Table 3. *Interatomic distances*

	V_2C
V–C	(3) 2·029 Å
C–C	(1) 2·288
V–V	(6) 2·836
	Ta_2C
Ta–C	(6) 2·186 Å
Ta–Ta	(3) 3·021
	(3) 3·080

the apices of a trigonal prism in V_2C, and forming one triangular face of the prism in Ta_2C. Thus V_2C, Ta_2C and Mo_2C have structures based on a hexagonal closest-packed metal lattice, with the carbon atoms filling one half of the octahedral holes, randomly in V_2C and in different ordered arrangements in Ta_2C and Mo_2C.

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Structural Changes Caused by the Neutron Irradiation of σ Phases

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The effect of fast neutron bombardment on the structure of three σ phases, MoRe55, MoRe68 and WRe50, has been studied by X-ray diffractometry. Radiation damage consisting of (i) line broadening, (ii) changes in unit-cell dimensions and (iii) disordering were observed, the magnitude of the effects depending on the total fast-neutron dose. It is suggested that the irradiation creates clusters of defects causing line broadening and that the change in unit-cell size is caused by the disordering of atoms of different radii.

Introduction

The study of the effect of fast-neutron irradiation of alloys has been mainly confined to simple cubic structures such as Cu_3Au (Adam, Green & Dugdale, 1952, Blewitt & Coltman, 1954), $MnNi_3$ (Aronin, 1954), Fe_3Al (Saenko, 1964), *etc.*, the interest being in the disordering or ordering produced. In the irradiation of some uranium-based alloys phase transformations have been reported (Konabeevsky, Pravdyuk & Kutaitsev, 1956; Bleiberg 1959). Enhanced precipitation with consequent changes in mechanical hardness have also been reported (Kernohan, Billington & Lewis, 1956). Incidental to these effects have been changes in lattice parameter and increased lattice strain, but the importance of the relation of crystal structure to the nature of the radiation damage has not been emphasized except in the special case of uranium growth (Cottrell, 1960) and more recently with BeO (Yakel & Borie, 1963). In view of the importance of focusing collisions (Goland, 1962), which involve the preferential deposition of energy along simple crystallographic directions (Gibson, Goland, Milgram & Vineyard, 1960), the effect of fast neutron irradiation on crystal structures is of considerable interest.

The binary σ phases, which have a complex body-centred tetragonal structure, are formed from transition elements in the third, fourth and fifth periods of the periodic table. This phase is associated with a large value of mechanical hardness coefficient and since the phase may be present in some reactor materials the mechanical changes caused by neutron irradiation are important. The nature of the crystalline changes accompanying the radiation damage forms the substance of this investigation.

Experimental

Small powder samples of the σ phase MoRe having compositions Mo 45 at.%, Re 55 at.% and Mo 32 at.%, Re 68 at.%, together with samples of σ-WRe having a composition W 50 at.%, Re 50 at.%, were irradiated *in vacuo* in aluminum cans in the reactor DIDO at the Atomic Energy Research Establishment, Harwell. Integrated doses of 8×10^{19} and 2×10^{20} fast neutrons were given to separate samples of each alloy maintained at the ambient reactor temperature approximately of 70 °C. The integrated slow neutron dose accompanying the fast dose was approximately the same. Flat diffractometer specimens were prepared from the irradiated samples for use on a Hilger instrument provided with a bent quartz crystal to give monochromatized Cu $K\alpha$ radiation and using a proportional counter as detector. This arrangement was used for producing X-ray diffraction records of the unirradiated specimens reported earlier (Wilson, 1963).

Results

The diffractometer traces of all three specimens showed evidence of radiation damage consisting of a general reduction in line intensities, line broadening and small displacements of the line positions. The two MoRe alloys showed further evidence of damage in the disappearance of several weak lines and irregular changes in the relative intensities of others. The severity of the radiation damage was much greater in the samples

Table 1. *Line broadening*

	Line widths at half-intensity (2θ in minutes)			Change in line widths (2θ in minutes)	
hkl	Unirradiated	Irradiated (Low dose)	Irradiated (High dose)	Irradiated (Low dose)	Irradiated (High dose)
			MoRe55		
002	13·68	11·82	15·00	−1·86	+1·32
330	13·20	11·76	13·92	−1·44	+0·72
212	15·42	14·88	17·04	−0·54	+1·62
411	15·00	14·70	16·56	−0·30	+1·56
331	15·18	14·82	19·50	−0·36	+4·32
312	16·08	14·34	18·96	−1·74	+2·88
532 631	10·20	8·52	12·72	−1·68	+2·52
721	8·16	9·48	12·72	+1·32	+4·56
			MoRe68		
002	12·00	10·62	15·60	−1·38	+3·60
330	13·80	—	16·50	—	+2·70
202	16·74	14·82	16·80	−1·92	+0·06
212	16·20	13·02	17·76	−3·18	+1·56
411	17·88	14·52	17·17	−3·36	−0·71
331	16·80	13·32	16·26	−3·48	−0·54
312	12·78	15·60	16·08	+2·82	+3·30
631 532	11·16	8·10	11·70	−3·06	+0·54
721	7·92	8·34	11·46	+0·42	+3·54
			WRe50		
002	8·40	10·08	11·82	+1·68	+3·42
330	13·98	10·62	15·90	−3·36	+1·92 *
202	12·00	11·88	16·98	−0·12	+4·98
212	16·50	12·24	16·74	−4·26	+0·24
411	15·12	12·42	16·08	−2·70	+0·96
331	14·10	13·50	16·86	−0·60	+2·76
312	13·20	14·40	15·30	+1·20	+2·10
631 532	8·58	9·18	11·52	+0·60	+2·94
721	9·60	9·00	13·98	−0·60	+4·38

* lines overlap.

Table 2. *Changes in unit-cell dimensions*

σ phase	Neutron dose (nvt)	Unit cell a(Å)	c(Å)	Volume (Å^3)	$\Delta aa \times 10^4$	$\Delta cc \times 10^4$	$\Delta VV \times 10^4$
MoRe 55	Unirradiated	9·6028	4·9833	459·529	—	—	—
	8×10^{19}	9·5903	4·9985	459·731	−13·02	+30·50	+ 4·41
	2×10^{20}	9·5840	5·0048	459·706	−19·58	+43·15	+3·86
MoRe 68	Unirradiated	9·5719	4·9765	455·953	—	—	—
	8×10^{19}	9·5650	4·9874	456·293	−7·21	+21·90	+7·13
	2×10^{20}	9·5617	4·9932	456·509	−10·66	+35·56	+12·19
WRe 50	Unirradiated	9·6285	5·0133	464·770	—	—	—
	8×10^{19}	9·6282	5·0150	464·902	−3·12	+3·39	+2·77
	2×10^{20}	9·6208	5·0323	465·789	−8·00	+37·9	+21·85

Table 3. *Values of* $\sin^2 \theta$ *and relative intensities of lines*

	LOW NEUTRON DOSE														HIGH NEUTRON DOSE													
σ-phase	MoRe55					MoRe68					WRe50				MoRe55					MoRe68					Wre50			
	$Sin^2\theta 10^4$		Intensities			$Sin^2\theta 10^4$		Intensities			$Sin^2\theta 10^4$		Intensities		$Sin^2\theta 10^4$		Intensities			$Sin^2\theta 10^4$		Intensities			$Sin^2\theta 10^4$		Intensities	
hkl	Unirr	Irrad	I_o	I_r	I_c	Unirr	Irra	I_o	I_r	I_c	Unirr	Irrad	I_o	I_r	Unirr	Irrad	I_o	I_r	I_c	Unirr	Irrad	I_o	I_r	I_o	Unirr	Irrad	I_o	I_r
101	303	302	10	4.3	25	-	-	7	2.5	12	-	-	-	3.2	-	-	-	2	12	-	-	-	8	43	-	-	-	5
111	367	366	-	0.7	4.5	-	-	-	0.4	3.2	-	-	-	-	-	-	-	-	2	-	-	-	1.3	11	-	-	-	-
311	883	882	8	14	7	888	885	7	8.5	4.1	876	876	9	11	883	885	7	7	3.5	888	888	33	29	14	876	878	12	15
002	955	949	38	51	58	959	951	22	29	34	942	944	26	38	955	947	18	25	29	959	953	98	100	119	942	938	43	53
112 410	1093	1097	166	210	195	1100	1099	115	121	116	1085	1090	168	157	1093	1090	127	102	97	1100	1103	419	418	402	1085	1088	195	221
330	1157	1160	93	92	87	1166	1165	52	54	49	1150	1153	67	70	1157	1164	44	45	43	1166	1165	164	186	169	1150	1156	65	99
202	1212	1207	83	81	73	1217	1211	46	47	43	1196	1198	68	61	1212	1208	34	39	36	1217	1211	180	165	150	1196	1195	93	86
212 420	1277	1272	152	163	156	1283	1276	105	95	90	1262	1262	90	123	1277	1273	66	80	77	1283	1276	258	330	312	1262	1257	145	172
411	1333	1333	249	247	255	1342	1340	135	144	146	1321	1325	200	187	1333	1337	113	120	125	1342	1342	521	498	507	1321	1326	233	262
331	1396	1398	110	119	121	1407	1405	57	69	74	1386	1389	90	88	1396	1402	54	58	61	1407	1406	254	240	258	1386	1390	85	124
222	1470	1466	32	28	28	1478	1472	21	16	17	1454	1454	23	22	1470	1452	36	14	14	1478	1472	65	56	60	1454	1451	44	32
312 430	1600	1595	33	34	37	1606	1603	18	19	21	1582	1583	23	25	1600	1598	22	17	18	1606	1601	81	67	71	1582	1580	31	35
322	1793	1790	9	8	12	1803	1798	6	4.6	6.2	1776	1776	7	5.8	1793	1791	5	4	6	1803	1804	23	16	21	1776	1769	9	8
501 431	1849	1853	12	9	13	1861	1859	8	5.4	6.2	1837	1841	9	6.4	1849	1856	6	4	7	1861	1860	22	17	21	1837	1840	8	9
511	1914	1914	9	8	12	1927	1923	6	4.6	7.6	1901	1902	6	5.8	1914	1921	4	4	6	1927	1924	25	16	26	1901	1903	9	8
521	2107	2111	6	3	5	2121	2119	3	1.8	3	2086	2093	4	2.2	2107	-	-	1.5	2.5	2121	-	-	6	10.2	2086	2094	3	3
432	2570	2567	8	8.5	4.5	2584	2580	5	4.9	2.4	2547	2542	6	6.5	2570	2561	4	4	2.2	2584	2586	20	17	8.3	2547	2544	8	10
611 512	2632	2631	9	8.7	4.6	2646	2645	7	5.5	4.2	2610	2602	6	6.3	2632	2627	4	4	2.3	2646	2647	22	19	14.5	2610	2604	13	9
621 522	2823	2821	16	19	15	2840	2828	10	11.4	8.4	2798	2799	11	14	2823	2818	6	9	8	2840	2826	42	37	29	2798	2798	23	20
631 532	3143	3144	51	50	44	3161	3152	33	29	25	3119	3117	37	37	3143	3145	19	24	21	3161	3159	92	100	86	3119	3118	79	53
550 710	3218	-	186	155	152	-	-	93	90	91	-	-	123	116	-		73	76	75	-	-	277	312	314	-	-	205	163
413	3243	3233				3261	3243				3208	3208			3243	3234				3261	3248				3208	3199		
602	3273	3272				3278	3281				-	-			3273	3273				3278	3289				-	-		
333	3307	3296				3325	3306				3271	3269			3307	3294				3325	3319				3271	3259		
612	3337	3336				3358	3347				3313	3310			-	-				3358	3355				3313	3310		
720	3412	3421	75	71	67	3433	3431	50	41	39	3390	3392	58	52	3412	3428	34	35	33	3433	3444	158	141	136	3390	3398	113	87
711 551	3459	3465				3478	3473				3434	3437			3459	3468				3478	3484				3434	3440		
622	3531	3532	17	13	14	3551	3539	9	7.7	7.8	3505	3502	12	10	3531	3529	22	15	16	3551	3555	34	27	27	3505	3501		
542	3596	3594	23	16	17	3613	3603	11	9.2	10	3566	3566	15	12	3596	3597				3613	3615	40	32	36	3566	3567	28	16
721	3649	3659	49	33	38	3675	3669	22	18	21	3627	3630	33	24	3649	3663	19	16	19	3675	3682	90	64	74	3627	3636	50	34
004 513	3823	3801	21	30	30	3838	3821	9	18	18	3774	3775	15	22	3823	3806	10	15	15	3838	3816	50	61	62	3774	3748	32	32

I_o = Observed intensity for irradiated specimens, I_r = Calculated intensity for random order
I_c = Calculated intensity for ordered unirradiated specimens

irradiated to the higher dose but the nature of the damage was similar in both samples.

(i) *Line broadening*

Measurements of line breadths at half intensity were made on the traces of several prominent well-shaped lines. The broadening produced is noted in Table 1. No attempt has been made to correct for instrument broadening since all the strong lines which were suitable for measurement suffer from some overlap from neighbouring lines, making accurate assessments of true line widths difficult. The small reduction in line width recorded for several low-dose samples is real and is believed to be caused by radiation-annealing of crystalline deformation produced in sample preparation. This effect is completely masked by the radiation damage effect in the high-dose specimens.

(ii) *Unit-cell dimensions*

The small line displacements observed were consistent with changes in the size of the unit cell of each specimen. The values of $\sin^2\theta$ were obtained from observations on as many high angle lines as possible and new values for a and c were determined with the use of the King & Massalki (1962) technique. The agreement between observed and calculated $\sin^2\theta$ values using the newly-found cell constants was remarkably good. The cell dimensions of the irradiated sample together with those of the unirradiated samples, all measured to an accuracy of $\pm 5\times10^{-4}$ Å, are given in Table 2. Irradiation causes a small expansion of the unit cell in each case as shown.

(iii) *Line intensities*

The relative intensities (I_c) and $\sin^2\theta$ values which were calculated to fit the unirradiated specimens reported earlier (Wilson, 1963), are given in Table 3. The intensities calculated for a random array of atoms in the σ-phase sites (I_r) are also given, all intensities being normalized with respect to observed totals. The line displacements are clearly indicated. Because of the similarity in X-ray scattering factors of W and Re each atom of the σ-WRe structure scatters X-rays almost equally so that the X-ray reflexions are virtually independent of the type of atom in each reflecting plane. Thus, this phase appears to be randomly ordered and, as expected, there is no significant change in this apparent random order given on irradiation. On the other hand, both σ-MoRe55 and σ-MoRe68 show marked reductions in the relative intensities of the weaker lines such as 101, 111, 311, *etc.*, which are consistent with a random arrangement of each structure. As shown in the earlier paper, the strong lines of the σ-phase structure are not sensitive to ordering but the intensities of many weak and very weak lines are critical in this respect. The changes in line intensity are dependent on the dose and for the low dose specimens the intensities correspond to a state between order and disorder. The agreement between the observed irradiated line and calculated random line intensities for the high dose specimens is good, but there are slight inconsistencies which are apparent in this comparison, even with σ-WRe, which may be associated with the detailed nature of the radiation damage produced which is not fully understood.

Discussion

Most of the crystalline damage effected by fast neutrons is caused by primary knock-on lattice atoms displaced by the colliding neutrons which produce interstitials and vacancies in the lattice. These point defects tend to anneal out at a rate determined by their mobility at the irradiation temperature. This simple concept leads to a volume change in the irradiated crystal dependent on whether an excess of vacancies or interstitials is ultimately produced. A dilatation of the unit cell is observed in several pure metals and alloys having simple crystal structures, *e.g.* f.c.c. Mo (Adam & Martin, 1958) and, likewise, b.c.c. Fe_3Al (Saenko). With high neutron doses the clustering of point defects can occur, leading to line broadening which is often observed. The change in order observed in several alloys such as Cu_3Au (Adam, Green & Dugdale), is believed to be caused by replacement collisions; these were initially conceived by Kinchin & Pease (1955) as displacement spikes but are now regarded as a correlation effect caused by focusing collisions. All these defects have been given a theoretical basis by the machine calculations of Gibson, Goland, Milgram & Vineyard.

The most significant feature of the damage observed in the MoRe and WRe σ phases is the expansion along the **c** direction and the contraction along the **a** direction. The relative change $\Delta c/c$ is always greater than $\Delta a/a$ and both changes are similar in magnitude to those reported for other alloy irradiations such as Fe_3Al (Saenko). In order to understand the anisotropic changes the σ phase might be considered as a layer structure comprising atoms in $A(0,0,0)$, $B(x,x,0)$, $C(x,y,0)$ and $D(x,y,0)$ sites. In each layer the network contains hexagons which lie in antisymmetric positions above each other in the stacking sequence adopted by the structure. The E-type atoms $(x,x,\frac{1}{4})$ form vertical rows threading the hexagons of the horizontal layers. There is no correlation between the broadening of particular lines on the diffractometer traces which can be associated with random changes in the stacking sequence and an anisotropic lattice expansion, such as were noted in the investigation of irradiated BeO (Yakel & Borie). The symmetrical nature of the line broadening observed for the large-dose specimens suggests a uniform concentration of defect clusters. The extremely small line broadening observed for the low dose specimens suggests that clusters were not produced in these samples and lattice changes were caused by point defects only. Both σ-ReMo55 and σ-ReMo68 were in the ordered state prior to irradiation and the effect of irradiation was to destroy this order to an extent dependent on the neutron dose. The change in order involves the redistribution of atoms of different size ($r_{\mathrm{Mo}}=$ 1·40 Å and $r_{\mathrm{Re}}=1{\cdot}37$ Å) among the *A*, *B*, *C*, *D* and *E* sites in the unit cell, which suggests a possible explanation for the observed lattice changes. Since the interatomic distances in the horizontal layers of the lattice approximate to the sum of the radii of the individual atoms the horizontal dimensions of the unit cell will be mostly governed by the sizes of the individual atoms, as is reflected in the values of *a* for various σ phases, *e.g.* in $\mathrm{Nb_3Os_2}$ $a=9{\cdot}858$ Å, in $\mathrm{Nb_3Ir_2}$ $a=9{\cdot}86$ Å, in $\mathrm{Mo_{19\cdot5}Os_{10\cdot5}}$ $a=9{\cdot}615$ Å, and the atomic radii are $r_{\mathrm{Nb}}=$ 1·47, $r_{\mathrm{Os}}=1{\cdot}34$, $r_{\mathrm{Ir}}=1{\cdot}35$, $r_{\mathrm{Mo}}=1{\cdot}40$ Å. In all three examples the ordering involved is very similar in nature (Spooner & Wilson, 1964). In each horizontal layer of the unit cell there are 1*A*, 2*B*, 4*C* and 4*D* sites and the numbers of each metal atom in the ordered and random states for σ-ReMo55 are given in Table 4.

Table 4. *Numbers of* Re *and* Mo *atoms in ordered and random states in* σ-ReMo55

	Ordered		Random	
Atom site	Re	Mo	Re	Mo
A	2	Nil	1·1	0·9
B	1	3	2·2	1·8
C	4	4	4·4	3·6
D	6·5	1·5	4·4	3·6
Total	13·5	8·5	12·1	9·9

There is thus a reduction in the relative number of smaller atoms (Re) in these layers, and this would suggest an overall increase in *a* which is not observed.

The interatomic distance between the atoms in *E* sites, which form the vertical rows, is given by $d_{EE}=c/2$ and it is a characteristic feature of the σ phase that this distance is much less than the sum of the radii of the atoms in these sites. For the three σ phases $\mathrm{Nb_3Os_2}$, $\mathrm{Nb_3Ir_2}$ and $\mathrm{Mo_{19\cdot5}Os_{10\cdot5}}$, the values of d_{EE} are 2·532, 2·525 and 2·471 Å, respectively, and since the occupancy of the sites is predominantly that of the major constituents Nb and Mo, whose diameters are 2·94 Å and 2·80 Å respectively, the contraction involved is considerable, amounting to approximately 15%. The nature of this bond between *E*-type atoms is unknown but it is extremely important in determining the value of *c*; for example in the σ phase $\mathrm{Nb_{13\cdot5}Re_{16\cdot5}}$, for which $a=9{\cdot}789$ and $c=5{\cdot}099$ Å there are only $4\frac{3}{4}$Nb in *E* sites (Spooner & Wilson). The larger number of Nb atoms in the *E* sites of $\mathrm{Nb_3Os_2}$ gives rise to a value of $c=5{\cdot}064$ Å which is smaller than that for $\mathrm{Mo_{13\cdot5}Re_{16\cdot5}}$ even though $r_{\mathrm{Nb}}>r_{\mathrm{Re}}$. It is suggested that a 'chemical' effect between Nb and Re atoms is responsible for a change in the binding of the *E*-site atoms when Os is replaced by Re causing an increase in *c*.

When the order of either ReMo σ phases is destroyed there is an increase of 1·4 atoms in the Re content of *E* sites and the disturbance of the binding involved might account for the corresponding increase in *c* observed after irradiation. Apart from the unusually short *E–E* bonds all the other interatomic distances involved in the 14-coordination of this site are commensurate with the sum of the appropriate atomic radii. Thus, it may be supposed that the 'size' effect governs the remainder of the coordinations and the replacement of Mo by Re would reduce the corresponding interatomic distances. Since there are 8 *E*-type sites contained in each unit cell the overall reduction in the non-vertical coordinations of these sites might give rise to a contraction in the *a* dimension greater than the expansion expected from the change in order *within* the layers. It is difficult to estimate the values of Δc and Δa caused by re-ordering without a more detailed knowledge of the *E* bond between *E–E* atoms. The explanation is also applicable to σ-WRe, but unfortunately there is no knowledge of the order involved in this phase.

It is interesting to compare this effect with the growth of α-uranium which is caused by neutron irradiation. The growth of α-uranium is associated with the low symmetry of the lattice and the covalent type of bonding between atoms contained in corrugated sheets. This covalent type bonding is also evidenced by abnormally short interatomic distances between particular atoms in the α-uranium lattice. Cottrell (1960) has explained the anisotropic growth of α-uranium by involving the thermal spike concept in which localized volumes of the lattice receive sufficient energy from radiation bombardment to become molten for very small time intervals. The strongly anisotropic expansion, produced in the manner suggested by Chebotarev (1961), gives rise to compensatory forces which cause displacement leading to the observed growth. Growth has not been measured in the irradiation of σ phases but the nature of the ordering forces responsible for the *E–E* site bond is undoubtedly connected with the anisotropic parameter changes derived from similar displacement spike considerations. It is hoped that the damage effects produced in other ordered sigma phases will shed more light on this phenomenon.

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Phases Cubiques Type Th_3P_4 dans les Sulfures, les Séléniures et les Tellurures L_2X_3 et L_3X_4 des Terres Rares, et dans leurs Combinaisons ML_2X_4 avec les Sulfures et Séléniures MX de Calcium, Strontium et Baryum. Formation et Propriétés Cristallines

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A survey has been made of the crystal structures of the rare earth sulfides, selenides and tellurides of composition L_2X_3, of compounds of composition L_3X_4 and L_2X_3 having the Th_3P_4 structure type, and of the existence of homogeneity ranges between these two limits of composition; also of the crystal structures of the ML_2X_4 compounds (L = rare earth, M = Mg, Ca, Sr, Ba and X = S or Se), of the Th_3P_4-type compounds of this composition and of homogeneity ranges between ML_2X_4 and L_2X_3. It was not possible to prepare definite compounds of composition MgL_2S_4, MgL_2Se_4 or CaL_2Se_4 with the first elements of the rare earth series but domains of homogeneity exist between these and L_2X_3.

En 1949, Zachariasen (1948, 1949) a établi que le sulfure Ce_2S_3 possédait le type structural Th_3P_4. Dans cette structure cubique à faces centrées qui appartient au groupe d'espace $I\bar{4}3d$ (T_d^6), les atomes métalliques ont les positions $12(k)$ des tables internationales, et les atomes de métalloïde les positions $16(f)$. Zachariasen a montré que, dans Ce_2S_3, les atomes de soufre occupent tous les sites du réseau des anions, et que le réseau des atomes de cérium est lacunaire, avec distribution désordonnée des lacunes. Il y a dans ces conditions $\frac{16}{3}$ de molécules Ce_2S_3 par maille cubique.

Depuis 1954, nous avons étudié les sulfures, séléniures et tellurures formés par tous les éléments des terres rares, ainsi que leurs combinaisons avec les sulfures, les séléniures et les tellurures d'autres éléments métalliques. De nombreux composés, parmi ceux que nous avons isolés, possèdent le type structural Th_3P_4. De plus, des domaines d'homogénéité importants ont également ce type cristallin. Le présent mémoire leur est plus spécialement consacré.

Nous joindrons, dans cette étude, l'yttrium et le scandium aux éléments des terres rares. En effet, lorsque l'on intercale ces éléments dans la série des terres rares en des places correspondant à leur rayon ionique, on ne constate aucune discontinuité dans l'ensemble des propriétés physico-chimiques et structurales des composés considérés. L'yttrium a généralement sa place au voisinage de l'holmium. Le scandium se place naturellement après le dernier élément des terres rares, puisque son rayon est nettement plus petit.

Composés L_2X_3 (L = terre rare, Y, Sc; X = S, Se ou Te)

Les sulfures et les séléniures sont préparés par action de l'hydrogène sulfuré ou de l'hydrogène sélénié sur les oxydes de terre rare vers 1200–1300 °C, dans des fours à induction haute fréquence. Cependant, avec les éléments de tête de la série des terres rares, on obtient ainsi le polyséléniures L_2Se_4 qu'il est ensuite nécessaire de dissocier ultérieurement par chauffage sous vide (Guittard, Benacerraf & Flahaut, 1964). Les tellurures sont préparés par union directe des éléments en ampoule scellée sous vide, vers 1000 °C.

De nombreux types cristallins ont été observés pour les composés stoechiométriques L_2X_3, dont la répartition est donnée dans le Tableau 1. De plus, en dehors de ces composés, existent des phases non stoechiométriques de type Th_3P_4 de compositions voisines de L_2X_3