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Ternary Tungsten Oxides with the Mo_5O_{14} Structure

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Following the discovery of a ternary Ge–W oxide with the Mo_5O_{14} structure, a large number of ternary M–W–O systems were surveyed to investigate the frequency of occurrence of this structure type. Samples were prepared by heating tungsten oxides and the appropriate ternary element or a suitable compound of the ternary element in evacuated silica ampoules at 1373°K for 1 week. The compositions investigated were close to $M_{0.02}W_{0.98}O_{2.80}$. Oxides with the Mo_5O_{14} structure were found in many systems across the whole of the periodic table, from Li to Bi. Some aspects of the formation of these phases and the way in which they could affect the course of reduction of WO_3 to W metal are discussed.

Introduction

The so-called θ molybdenum oxide Mo_5O_{14} was first studied in detail by Kihlborg (*1*, *2*), who investigated the conditions under which it formed and also determined its structure. The results of these investigations showed that the oxide was metastable and decomposed at temperatures above about 820°K. Its structure, shown in Fig. 1, is made up of corner-sharing octahedra and groups of five MoO_6 octahedra surrounding a seven-coordinated Mo atom, called pentagonal columns (*PC*s). These two units are linked so as to produce a structure which also contains pentagonal and hexagonal tunnels, which in the binary oxide are empty. The structure can be readily derived from a fully oxidized parent structure of the ReO_3 type by the elegant geometrical operation of rotary shear (*3*), but it is not certain that such a transformation does take place in real crystals.

Although the binary Mo_5O_{14} oxide is metastable, Kihlborg discovered that partial substitution of molybdenum by other elements could improve its stability (*4*). Subsequently, Ekström made a systematic study of the substitution of Mo by other elements in the Mo_5O_{14} structure and determined the substitution ranges and stabilities of a number of these ternary oxides (*5*–*8*) which we will denote as $\theta_{Mo}(M)$ phases here. The results of these and similar studies on other related molybdenum and tungsten oxides have also been surveyed and reviewed critically by Ekström (*9*), who found that only a few elements (Ti, V, Nb, Ta, and W) were able to substitute into the Mo_5O_{14} structure, that the degree of substitution was generally small, and that the Mo_5O_{14} structure was stabilized by only a few hundred degrees above the binary oxide in most cases. The enhanced stability of these ternary oxides over that of the parent binary oxide was explained in terms of the electron concentration in the structures, particularly within the *PC*s themselves (*9*).

As part of a systematic survey of phases occurring in the WO_3 neighborhood of a number of ternary M–W–O oxides (*10*–*14*) an oxide isostructural with Mo_5O_{14} was found in preparations of composition close to $Ge_2W_{16}O_{49}$ (*15*). Further experiments are now in progress to determine the existence range of this material. As the phase formed

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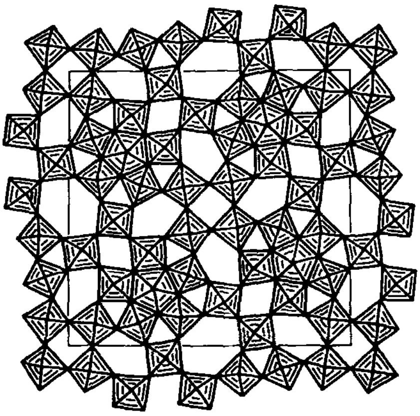

FIG. 1. The structure of Mo_5O_{14} projected onto (001).

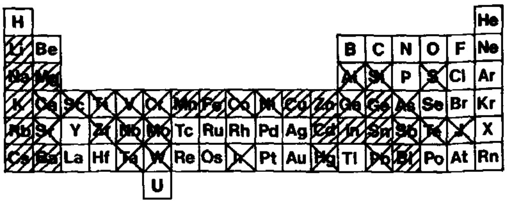

FIG. 2. Diagram showing the elements investigated in the present study. Those forming a $\theta_W(M)$ phase are shaded while those which do not form a $\theta_W(M)$ phase have a cross through the element's symbol.

readily at temperatures of the order of 1373°K, far above the decomposition temperatures of the known ternary $\theta_{Mo}(M)$-oxides, the reasons for its increased stability compared to these latter phases are of some interest. In addition, it is also of interest to determine whether other elements can give rise to analogous ternary $\theta_W(M)$-oxide structures, both because such phases may play an important part in the path of reduction of WO_3 containing metallic impurities to lower oxides or W metal and also because a comparison with the well-studied $\theta_{Mo}(M)$-oxides may shed light on the factors which control the interplay of structure and stability in these oxides. Because of this, we have made a series of preparations in the composition range expected to yield ternary $\theta_W(M)$-oxides, using metal dopants from a wide range of the periodic table. The present paper surveys these results and discusses the factors which may be important in stabilizing this particular structure type.

Experimental

The elements investigated in this study are shown in Fig. 2. All preparations were made by weighing mixtures of the appropriate second metal or a suitable oxide with WO_3 powder and WO_2 powder or W metal. The WO_3 was either of Specpure grade (from Johnson Matthey Ltd.) or prepared by heating tungstic acid (from Matheson, Coleman and Bell, p.a.) in air for several days at about 1073°K. The WO_2 was prepared by reduction of the WO_3 in a stream of hydrogen–water gas mixture at 1023°K. To obtain a suitable partial pressure of water vapor, the hydrogen was allowed to bubble through water at a temperature of 358°K. The degree of reduction of the WO_3 was checked by weighing and inspection of X-ray powder photographs. Tungsten metal was used in the form of chips turned from a rod of Specpure tungsten metal (from Johnson Matthey Ltd.). The second metals and oxides were of Specpure grade (from Johnson Matthey Ltd.) or else of analytical grade (from Baker Chemical Co., Allied Chemical & Dye Co., or E. Merck AG).

The weighed mixtures were of gross compositions given by the formulas $M_{0.02}WO_{2.80}$ or $M_{0.02}W_{0.98}O_{2.80}$ for all elements. The mixtures so prepared were sealed in evacuated silica ampoules and heated for 1 week at 1373°K. In addition, the systems containing Ti, Zr, V, Nb, Ta, Cr, W, Mn, Fe, and Ge were investigated in detail over a large range of compositions and temperatures which include the $(M,W)O_{2.72}$ and $(M,W)O_{2.80}$ lines in the 1373°K phase diagram. Some of these investigations have been published and can be referred to for further details of compositions examined (*9–15*), while results on the Fe-, Mn-, and Ge–W–O systems will be published in the near future. After heat treatment the samples were removed from the furnaces and allowed to cool to room temperature without special quenching techniques being employed.

All samples were investigated by recording their X-ray powder patterns at room temperature in a Guinier–Hägg focusing camera using $CuK\alpha_1$ radiation ($\lambda = 0.154051$ nm) and KCl ($a = 0.62919$ nm) as an internal standard. The positions of the lines on the film were determined either visually or by means of an automatic Abrahamsson film scanner (*16*). Evaluation of the film data and indexing and refinement of the unit cell parameters by least-squares techniques were performed on an IBM 1800 computer, using programs written by Werner (*17*). In addition, many samples were studied by optical and electron microscopy. Optical microscopy was carried out with a Zeiss Ultraphot optical microscope and electron microscopy with a JEM 100B electron microscope operated at 100 kV and fitted with a goniometer stage. Electron microscope specimens were prepared by crushing samples in an agate mortar and dispersing the resultant fragments in *n*-butanol. A drop of the suspension was allowed to dry on a net-like carbon film resting on a conventional copper support grid. Crystal flakes over holes in the carbon film were chosen for study.

Results

Figure 2 shows both the elements investigated and those which form a $\theta_W(M)$-oxide after heating for 1 week at 1373°K. The samples were rarely monophasic, but other compounds present in any particular sample were not studied in detail and Fig. 2 records only the presence or absence of the Mo_5O_{14} structure type in the preparations. It is of note that the rate of reaction in these experiments varied widely, depending upon starting products. For example, the θ_W(Ge)-oxide was readily obtained in samples prepared from Ge metal while reactions with GeO_2 apparently did not take place at all. Similarly, in the ternary Ta–W–O system, compositions made with Ta metal were unreactive while those with Ta_2O_5 reacted rapidly, although in this case a θ_W(Ta)-oxide was not formed. In the present series of experiments, both oxide and metal forms of the third element were used whenever possible in order to eliminate a null result due to factors of this type.

In all systems where a $\theta_W(M)$-oxide was identified by X-ray powder diffraction in the preparations, a refinement of the unit cell parameters was made. It was found that the lattice parameters did not vary very much from the values $a = 2.329$ nm, $c = 0.3794$ nm for the tetragonal unit cell which seems reasonable in view of the fact that the amount of the second metal, M, was only about 2 at% in these samples and thus any effect upon the cell dimensions would be expected to be low. The use of a film scanner made it possible to compare the relative line intensities for the group of X-ray powder patterns that appeared to be of monophasic $\theta_W(M)$-oxides or contaminated with only minor amounts of other oxides viz., M = Na, K, Cu or Ba. No significant shifts in intensities were observed, which is also possibly due to the low concentration of the metal M present.

A comparison of the X-ray powder patterns of the $\theta_W(M)$ phases with the X-ray powder patterns of the $\theta_{Mo}(M)$-oxides showed some differences in the line of intensity distribution

TABLE I

THE X-RAY POWDER PATTERN OF A θ_{Mo}(V)-OXIDE OF COMPOSITION $(V_{0.07}Mo_{0.93})_5O_{14}$[a]

d_{obs} (nm)	I_{obs}	$h\,k\,l$	$\lvert F\rvert^2_{obs}$	$\sin^2\theta_{obs} \times 10^5$	Δ
1.139	475	2 0 0	39	457	+3
1.022	386	2 1 0	40	568	0
0.7214	187	3 1 0	40	1140	+3
0.6330	61	3 2 0	17	1480	+2
0.5707	129	4 0 0	46	1821	+2
0.5542	33	4 1 0	11	1931	−2
0.5380	314	3 3 0	127	2050	+3
0.5109	46	4 2 0	20	2272	−2
0.4480	41	5 1 0	24	2955	−2
0.4238	87	5 2 0	58	3302	+4
0.4036	149	4 4 0	112	3672	+3
0.3991	1645	0 0 1	1275	3724	−3
0.3916	14	5 3 0	11	3869	+2
0.3807	511	6 0 0	436	4094	0
0.3752	236	6 1 0	207	4213	+5
0.3609	143	6 2 0	136	4555	+6
0.3567	1095	5 4 0	1074	4662	−1
0.3492	23	3 1 1	23	4864	0
0.3403	169	6 3 0	183	5121	+3
0.3269	65	4 0 1	77	5553	+6
0.3228	282	7 1 0	343	5693	+7

Table I continued

TABLE I (*continued*)

d_{obs} (nm)	I_{obs}	$h\ k\ l$	$\|F\|^2_{obs}$	$\sin^2\theta_{obs} \times 10^5$	Δ
0.3205	70	3 3 1	86	5775	+1
0.3166	319	6 4 0	405	5918	+4
0.3001	55	7 3 0	78	6587	−9
0.2924	15	6 5 0	22	6938	0
0.2906	22	5 2 1	33	7027	+2
0.2853	136	8 0 0	216	7287	+8
0.2834	754	8 1 0	1217	7388	−5
0.2769	93	8 2 0	157	7737	+3
0.2755	186	6 0 1	320	7817	−4
0.2735	112	6 1 1	195	7928	−7
0.2692	107	6 6 0	193	8189	0
0.2676	92	6 2 1	168	8285	−2
0.2659	528	5 4 1	980	8392	+2
0.2653	25	7 5 0	48	8426	+10
0.2589	74	6 3 1	145	8850	+5
0.2509	93	7 1 1	195	9421	+7
0.2481	109	6 4 1	235	9644	+3
0.2466	98	7 2 1	213	9755	0
0.2397	25	7 3 1	58	10316	−8
0.2322	51	8 0 1	126	11012	+6
0.2310	251	8 1 1	630	11122	+2
0.2275	42	8 2 1	108	11453	−8
0.2231	18	6 6 1	52	11922	+6
0.2210	52	7 5 1	143	12141	−2
0.2149	32	8 7 0	93	12862	+10

[a] Data were recorded at room temperature using a Guinier–Hägg camera with strictly monochromatic Cu$K\alpha_1$ radiation. The observed integrated intensities I_{obs} were obtained by a film scanner process and the corresponding $|F|^2_{obs}$ values after correction for polarization, Lorentz, and geometric factors were obtained by computer routines (*16*, *17*). A refinement of the tetragonal subcell parameters gave $a = 2.2839 \pm 1$ nm and $c = 0.3990 \pm 1$ nm. In the table, $\Delta = 10^5 \times (\sin^2\theta_{obs} - \sin^2\theta_{calc})$.

between the two which can be seen from Tables I and II. This difference is expected as the change in the average metal atom number between a $\theta_{Mo}(M)$- and $\theta_W(M)$-oxide is appreciable and the effect upon the X-ray scattering power for the diffracted X-ray beams is also significant. Another difference between the $\theta_{Mo}(M)$-oxides and the $\theta_W(M)$-oxides is that the metal atom layer in the former oxides is puckered (*9*). This gives rise to an orthorhombic superstructure with an *a*-axis of twice the tetragonal *a* dimension (*18*), and causes

TABLE II

THE X-RAY POWDER PATTERN OF AN APPARENTLY MONOPHASIC θ_W(Na)-OXIDE RECORDED FROM A SAMPLE OF GROSS COMPOSITION $Na_{0.02}WO_{2.80}$[a]

d_{obs} (nm)	I_{obs}	$h\ k\ l$	$\|F\|^2_{obs}$	$\sin^2\theta_{obs} \times 10_5$	Δ
1.165	306	2 0 0	24	437	0
1.042	175	2 1 0	17	546	0
0.7366	117	3 1 0	24	1094	+1
0.6456	24	3 2 0	6	1423	+3
0.5822	81	4 0 0	28	1750	+2
0.5492	247	3 3 0	96	1968	+1
0.5210	62	4 2 0	27	2187	+2
0.4570	35	5 1 0	20	2845	+4
0.4327	36	5 2 0	23	3172	+3
0.4118	37	4 4 0	26	3498	+2
0.3884	411	6 0 0	337	3933	−1
0.3797	1711	0 0 1	1472	4114	−6
0.3680	81	6 2 0	74	4381	+10
0.3640	829	5 4 0	781	4478	−2
0.3607	44	2 0 1	42	4559	+2
0.3565	41	2 1 1	40	4668	+2
0.3473	202	6 3 0	210	4918	+1
0.3373	36	3 1 1	39	5214	+1
0.3296	279	7 1 0	325	5461	−2
0.3232	275	6 4 0	334	5680	−2
0.3200	189	7 2 0	235	5791	0
0.3180	32	4 0 1	40	5867	−1
0.3122	103	3 3 1	135	6087	0
0.3060	59	7 3 0	80	6325	−13
0.2913	147	8 0 0	224	6995	+2
0.2890	660	8 1 0	1022	7098	−4
0.2853	33	5 2 1	52	7285	−4
0.2825	69	8 2 0	112	7433	+3
0.2791	20	4 4 1	33	7616	0
0.2747	119	6 6 0	205	7865	−2
0.2714	450	6 0 1	799	8060	+6
0.2696	67	6 1 1	120	8164	+1
0.2626	687	5 4 1	1308	8597	−3
0.2562	159	6 3 1	319	9034	−3
0.2527	20	9 2 0	41	9292	+5
0.2488	209	7 1 1	447	9580	−3
0.2460	212	6 4 1	465	9802	0
0.2446	139	7 2 1	308	9910	−1
0.2382	46	7 3 1	108	10454	−4
0.2366	10	9 4 0	23	10596	−3
0.2345	16	6 5 1	38	10779	−6
0.2299	610	8 1 1	1546	11219	−3

[a] The pattern and the values have been obtained in the same way as described in Table I. A refinement of the tetragonal cell parameters gave $a = 2.2302 \pm 1$ and 0.3795 ± 1 nm. In the table, $\Delta = 10^5 \times (\sin^2\theta_{obs} - \sin^2\theta_{calc})$.

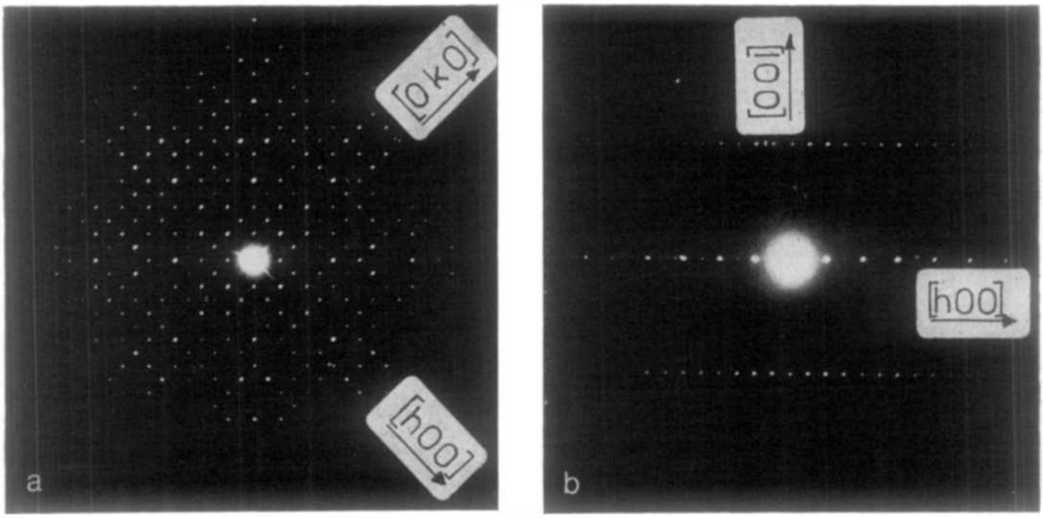

FIG. 3. (a) The *hk*0 electron diffraction pattern from a θ_W(Fe) oxide. (b) The *h*0*l* electron diffraction pattern from a θ_W(Ba) oxide.

the *c*-axis to be of the order of 0.395 nm. In the $\theta_W(M)$-oxides the *c*-axis is about 0.379 nm, which suggests that in these oxides the metal atoms are in a planar layer rather than a puckered one. A similar value, 0.378 nm, is found in the $W_{18}O_{49}$ oxide where it is known that the tungsten atoms all lie in a mirror plane (*19*).

This conclusion was supported by examination of electron diffraction patterns of the $\theta_W(M)$ oxides. In general, no evidence was found to indicate that the true unit cell was larger than that indicated by the X-ray results above, and all diffraction patterns could be successfully indexed in terms of a tetragonal cell of approximate dimensions $a = 2.3$ nm, $c = 0.38$ nm. Figure 3 shows *hk*0 and *h*0*l* sections through the reciprocal lattice. It must be remembered, however, that due to strong dynamical effects present in electron diffraction, spot intensities can vary a good deal from that expected on the basis of kinematical theory and the question of whether some of these $\theta_W(M)$ oxides do have larger unit cells due to puckering of the metal atom layer should remain open until careful single-crystal structure determinations have been made.

High-resolution micrographs of the *hk*0 projection of the structure, such as that shown in Fig. 4, showed that large crystals were almost always well ordered. Very few structural faults such as twins or irregular spacing or occupation of the *PC*s or tunnels were found. It was, however, noticed that crystal flakes often contained holes and this may be due to their mode of growth. Similar features have been seen in other crystals containing *PC*s, such as the tetragonal tungsten bronze structures of the Nb–W–O and Ta–W–O oxides.

Discussion

As the present study was envisaged as a general survey, many of the elements used have not been investigated in detail and to complete the study one should ideally extend the compositions studied as well as heating times and temperatures. Nevertheless, sufficient results have been obtained to allow some of the more important aspects of the formation of $\theta_W(M)$ phases to be outlined.

An examination of Fig. 2 shows no significant trends in the elements which do form $\theta_W(M)$ oxides from the point of view of chemical periodicity with two exceptions, the alkali metals which all form these oxides and the group of early transition elements of groups 4A, 5A, and 6A which appear not to

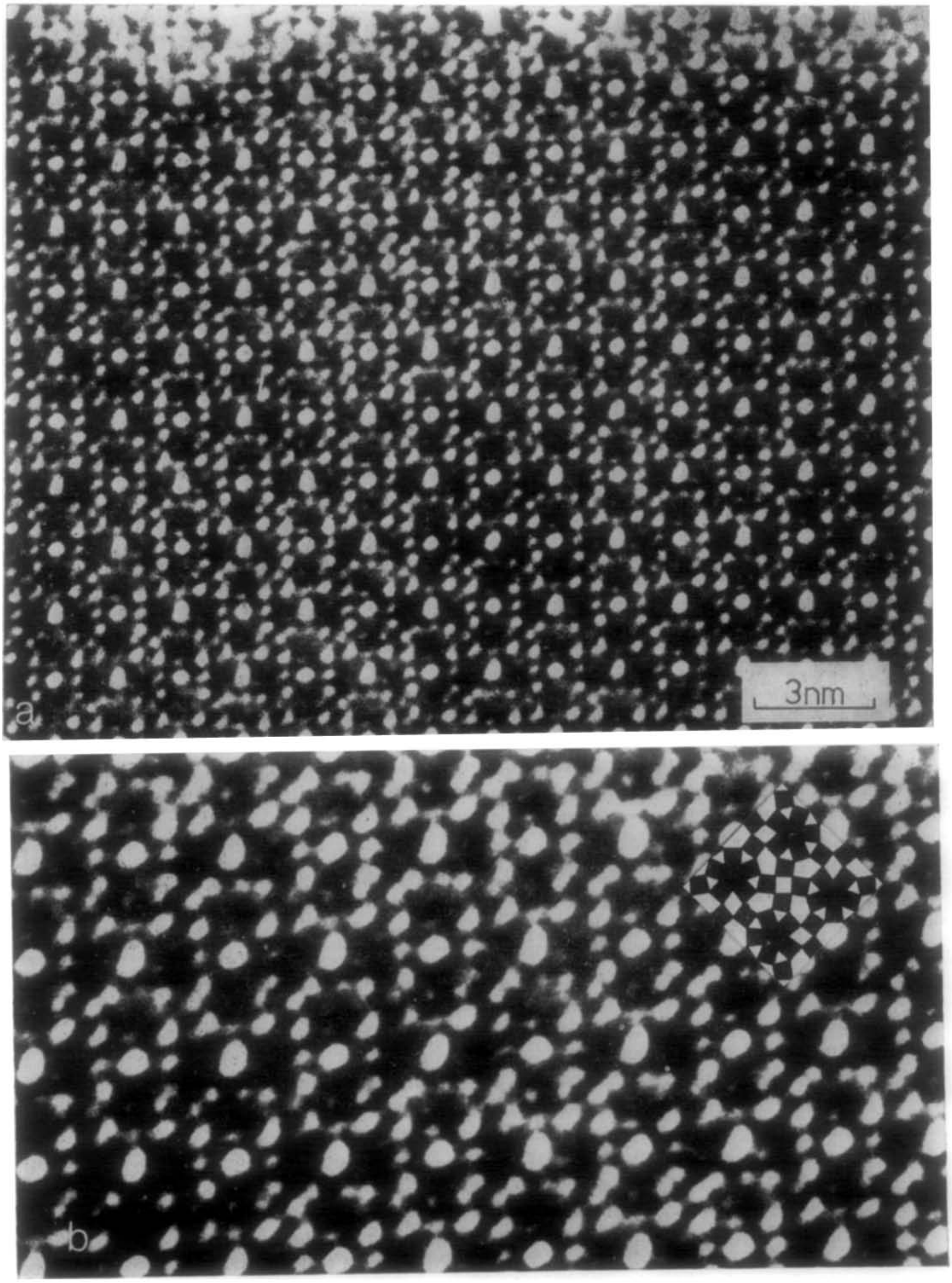

FIG. 4. (a) High-resolution lattice image of the structure of a θ_W(Fe) oxide viewed along [001]. (b) Higher magnification print of part of the same crystal flake as in (a) with the structure of Mo_5O_{14} superimposed, confirming the identity of the two structure types.

be able to initiate or take part in $\theta_W(M)$-oxide formation. Leaving the latter group of elements to one side for the moment, the most obvious feature of Fig. 2 is the wide diversity of elements which have some role to play in the formation of a $\theta_W(M)$ phase. The range is from the semimetals Bi, Sn, and Ge to the electropositive alkali metals, which indicates that neither ionic size nor a preference for pentagonal bipyramidal coordination seems to be a determining factor in the reaction.

This lack of any obvious correlation suggests that no one feature of the elements which form the $\theta_W(M)$-oxides is of overriding importance or significance and that different elements may have quite different roles to play in the formation reaction. It is therefore unlikely that only one formation mechanism will be found to apply over the whole of the periodic table or that only one mode of participation of the third element in the formation of the $\theta_W(M)$ structure will result. At present our data suggest that at least two different groups of elements can be identified.

The first group is comprised of those elements which do not appear to have a significant *structural* role to play in the $\theta_W(M)$ phases. Elements of this type have been characterized in some of the systems where a large number of compositions have been prepared and where a small amount of ternary metal, of the order of less than 1 at% serves to produce the θ_W-phase. Examples of this are Mn and Fe, but others are also likely to exist. With such a low amount of the third metal, it would seem unlikely that stabilization of the structure comes about by occupation of pentagonal sites in the *PC*s or by withdrawal of electrons from the conduction band in the structure in just sufficient numbers to stabilize the *PC*s, as has been suggested for the $\theta_{Mo}(M)$ oxides (*9*). A direct structural role would, instead, suggest that a certain specific percentage of ternary metal would be optimum in the formation reaction, either to achieve the correct electron balance, as has been suggested for some tungsten bronzes (*20*), or else to fill a minimum percentage of some favored site in the structure.

In terms of a phase diagram, observations suggest that many of the $\theta_W(M)$-oxides found to date have compositions which are very close to the WO_3–WO_2 line and fall into this group. Bearing in mind that many of the elements used in these trials need to be investigated further from this point of view, we are led to a conclusion that the observed θ_W-oxide may be characterized as a pseudo*binary* oxide, at least in the Fe–W–O and Mn–W–O systems. The role of the second metal in these systems may then be regarded in the light of a catalyst or promoter of the reaction, although we should stress here that we are of necessity forced to use these terms rather loosely until more information on the mechanism of formation of these phases is available.

The generalizations above are unlikely to apply to all the systems which form a $\theta_W(M)$ phase and a second group is typified by the Ge–W–O system (*15*) in which results suggest that rather large amounts of Ge are present in monophasic θ_W(Ge) crystals. Although single-crystal structural studies are desirable to give more information on the structural role of Ge in this phase, it does seem reasonable to conclude, therefore, that the Ge forms an integral and essential part of the structure. A similar situation is likely to hold for some of the other elements investigated as well. In these cases, the element *M* may substitute for W in the structure, to form $(M,W)_5O_{14}$ phases, or alternatively a bronze $M_xW_5O_{14}$ might be produced, with the *M* element occupying some of the available tunnel sites in the structure. In the former case, the composition would lie on the $(M_xW_{1-x})O_{2.80}$ line in the phase diagram while in the latter case the $M_xWO_{2.80}$ line would be followed. From the limited number of compositions prepared for most of the elements in this study no comprehensive conclusions can yet be presented upon this matter, or upon the part that the metal plays in the mechanism of formation of the phase. However, it is reasonable to suppose, using the known crystal chemistry of the tetragonal tungsten bronzes (*TTB*), that the larger elements, such as K, Sr, or Bi may well occupy some of the pentagonal tunnels in the $\theta_W(M)$-oxides. This conclusion is supported by the close relationship between the *TTB* and Mo_5O_{14} structure types (*9*) and from this point of view it would not be very surprising

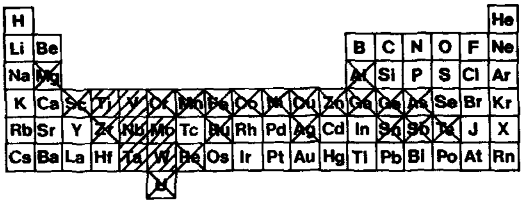

FIG. 5. Diagram showing the elements which substitute into Mo_5O_{14} to form ternary $\theta_{Mo}(M)$ phases (shaded) and those which do not form $\theta_{Mo}(M)$ phases (crossed), after (*9*).

if bronze phases having an Mo_5O_{14} host structure formed.

It is of some interest to compare Fig. 2 with the results of a similar survey on the stabilization of the analogous $\theta_{Mo}(M)$ oxides (*9*). These results are summarized in Fig. 5. The most noticeable feature is that the elements which are effective in stabilizing the θ_{Mo}-phase, the early transition elements of groups 4A, 5A, and 6A of the periodic table, do not appear to have any similar effect in the M–W–O systems. Until more data are available, a complete explanation of this difference cannot be made. However, one point can be made. In the $\theta_{Mo}(M)$ oxides, it was found that the ternary metal M substituted for Mo in compounds of general formula $(M_xMo_{1-x})_5O_{14}$ and that in general no alternative ternary M–Mo–O phases existed in similar regions of the phase diagram to the θ-phase (*9*). In the V, Nb, and Ta–W–O systems, on the other hand, we have previously found that all of the third metal seems to react rapidly to form stable ternary compounds, V_2WO_6 or a *TTB* phase (*13*, *14*). Thus, the difference in behavior between Mo and W may lie in the availability of alternate stable ternary oxides in the phase fields near to $MO_{2.80}$ which are preferred.

The present results have a bearing on the question of the reduction of WO_3, a procedure which is widely used to produce W metal powder and often forms a stage in the fabrication of W metal wires and foils. It has recently been shown that the morphology and particle size of the W powder formed by reduction of WO_3 are controlled by the size of $W_{18}O_{49}$ crystals, which are produced as an intermediate in the reduction reaction (*21*). It is also known that in the fabrication of tungsten products such as wires, a superior grain texture results if the WO_3 is doped with foreign metals such as K before reduction (*22*). Clearly, the presence of a $\theta_W(M)$ phase with a crystal habit different from $W_{18}O_{49}$ could, in principle, yield a different texture for the final W metal produced, as the course of the reduction reaction would be modified somewhat compared to the course of reduction in the binary system. For some purposes, this change could well be beneficial. A study of the reduction of doped WO_3 to W metal in systems which do support a $\theta_W(M)$ phase would therefore be of considerable interest, particularly in comparison with the pure oxide.

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