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The Crystal Chemistry of Kappa-Phases*

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A survey of compounds belonging to the kappa-phase structure family is made. The hexagonal crystal structure of the kappa-phases is composed of a metal atom sublattice of the Mn_3Al_{10} type, where the triangular–prismatic and/or octahedral interstices may be filled with *p* element or transition metal atoms to a varying extent. The results of crystal structure refinements from neutron powder and X-ray single-crystal diffraction data are used to analyze the atomic distribution on the various crystallographic positions and to discuss the compositions and homogeneity ranges for a number of kappa-phase representatives. © 1987 Academic Press, Inc.

1. Introduction

The name kappa-phase for the class of compounds discussed in the present survey is derived from a ternary phase in the system Co–W–C discovered by Rautala and Norton (*1*) more than 30 years ago and denoted by the Greek letter κ. Subsequent work as described below has revealed the occurrence of a large number of compounds belonging to the kappa-phase family and provided detailed crystallographic data on several representatives of the kappa-type structure.

The presently available information is almost exclusively based on the results obtained in two laboratories: Institute of Physical Chemistry, University of Vienna, and Department of Inorganic Chemistry, University of Uppsala. It seems most appropriate on the occasion of Professor H. Nowotny's 75th birthday to present a contribution on kappa-phase chemistry as a tribute to the scientific inspiration and stimulation that Professor Nowotny has provided—not only to the students in his own laboratory but also to scientists in many other countries and especially to the Solid State Chemistry research group in Uppsala.

2. General Structural Features of Kappa-Phases

It seems appropriate to start this survey by presenting the main features of the kappa-phase atomic arrangement, thus providing a useful basis for subsequent detailed discussions of compositions, homogeneity ranges, and atomic distribution. The following presentation of the kappa-phase crystallography is made in conjunction with a brief account of the research development behind present-day knowledge of kappa-phase crystal chemistry.

As already mentioned, the first represen-

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* Dedicated to Dr. H. Nowotny.

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tative of the kappa-phase family was reported by Rautala and Norton (*1*). The approximate composition was reported to be $Co_3W_{10}C_4$, and powder diffraction data indicated a hexagonal symmetry, with the lattice constants *a* and *c* nearly equal. Analogous phases were also found in the Fe–W–C, Ni–W–C, and Mn–W–C systems (*1, 2*). Schönberg (*3*) recorded X-ray powder diffraction intensities for kappa-(Co–W–C) and used the data for constructing a structure proposal. This was based on $P6_3/mmc$ space group symmetry, with 12 W on a 12*k* position, 6 W and 6 Co distributed randomly between two 6*h* positions, 6 C on 6*g* and 2 C on 2*c*, corresponding to the formula $Co_3W_9C_4$. The structure can be described with reference to Fig. 1 as follows. The figure shows the structure in projection on the basal plane. Connecting lines have been drawn only between atoms within the *z* range ± 0.25. The remaining half of the structure is obtained by reflection in a mirror plane perpendicular to *c* at $z = 0.25$.

The 12*k* and the 6*h*(II) atoms are arranged at the corners of deformed icosahedra. The centers of the icosahedra are at the 2*a* positions. Each icosahedron shares faces with two adjoining icosahedra to form infinite columns along the *c* axis. The columns are interconnected via octahedra, formed by 12*k* and 6*h*(I) atoms. The octahedra are centered at 6*g*. Furthermore, there are also trigonal–prismatic arrangements of 12*k* atoms, with the centers at 2*c*.

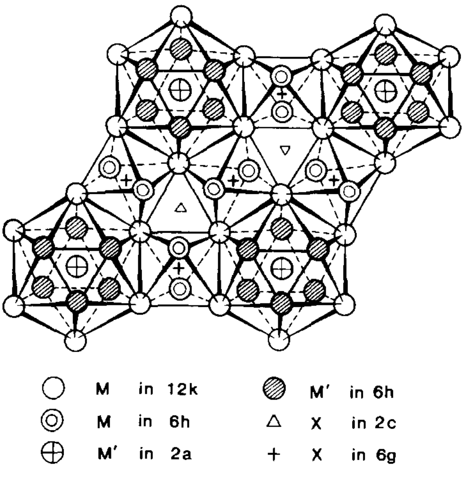

FIG. 1. The structure of the kappa-phase projected along the hexagonal axis. The ∇ position is situated at $z = 0.25$ and the △ position is situated at $z = -0.25$.

In Schönberg's structure proposal, the 2*a* icosahedral centers were assumed to be empty, while both the octahedral 6*g* and the trigonal–prismatic 2*c* interstices were assumed to be filled with carbon atoms. The similarity between Schönberg's structure and that of Co_4Al_{10} (*4*) was pointed out by Kripyakevich (*5, 6*), who noted that the kappa-(Co–W–C) structure can be derived by introducing carbon atoms into the trigonal–prismatic and octahedral holes of a defect Co_4Al_{10}-type structure lacking atoms in the icosahedral position 2*a* and the trigonal–prismatic position 2*c*. This relationship was also observed by Reiffenstein *et al.* (*7*) who, however, emphasized the close relationship between the metal atom sublattice of kappa-(Co–W–C) and the Mn_3Al_{10} structure (*8*), where, in contrast to the Co_4Al_{10} structure the trigonal–prismatic 2*c* site is empty. The metal atom sublattice of the kappa-carbide and Mn_3Al_{10} would then be identical, disregarding the empty icosahedral 2*a* site in the carbide according to Schönberg.

In a series of studies, Nowotny and coworkers (*7, 9–12*) prepared new kappa-phases in a number of ternary and quaternary systems, including borides, oxides, and phases containing three metallic components. They performed the first single-crystal structure determination of a kappa-phase by refining the kappa-(Hf–Mo–B) structure from Weissenberg photographic X-ray data (*10*). The following results were obtained: the 12*k* position is occupied by hafnium atoms, the distribution of hafnium and molybdenum atoms on the two 6*h* positions is completely ordered, molybdenum atoms occupy the 2*a* position, and boron atoms occupy the 2*c* position. For the kappa-phases formed by transition metal components only, e.g., the kappa-phases in the ternary systems Hf–Mo–{Fe, Co, Ni}, a distribution of the atoms similar to that in the kappa-borides was assumed, with iron, cobalt, or nickel replacing boron on the 2*c* site. For the kappa-oxides, on the other hand, it was suggested that the 2*c* position is empty and that the oxygen atoms occupy the octahedral 6*g* position (*11*).

By analogy with all these phases, Rogl and Nowotny (*11*) proposed that the ternary kappa-carbides also have a metal atom sublattice of the Mn_3Al_{10} type, with the icosahedral 2*a* hole filled, and an ordered distribution of the two types of metal atom on the two 6*h* sites. As far as the 2*a* icosahedral site is concerned, all subsequent crystal structure refinements of kappa-phases (*13–18*), including neutron diffraction investigations of the kappa-(Co–W–C) and kappa-(Fe–W–C) structures (*13, 16*), have shown unambiguously that it is always occupied by metal atoms. The degree of ordering as well as the degree of occupancy of the various crystallographic positions may well be variable, as is discussed in more detail in Section 5.

3. The Occurrence of Kappa-Phases

In addition to the kappa-phases containing carbon, work in Vienna revealed the existence of kappa-phases containing boron and oxygen (*7, 9–12*). Studies in Uppsala have later shown that kappa-phases are also formed in systems containing the nonmetals Si, P, S, Ge, As, and Se (*19–22*). Recently, the first kappa-phases with titanium as one of the transition metal components were found in the Fe–Ti–O and Mn–Ti–O systems (*18*). Presently known ternary and quaternary systems containing kappa-phases are collected in Table I. For each kappa-phase one set of values for the unit cell dimensions is given (as reported in the first of the references listed). It should be emphasized that most kappa-phases have a range of homogeneity and accordingly variable unit cell dimensions. The values quoted in Table I should therefore mainly be taken as a proof for the occurrence of kappa-phases in the various systems. For detailed information on the compositions and lattice parameter variations, the original references should be consulted. Phases related to the kappa-type structure, some of them having already been mentioned in the text (Co_4Al_{10}, Mn_3Al_{10}), are also included at the end of Table I.

In addition to the kappa-phases listed in Table I it has been reported that the kappa-(Hf–Mo–B) phase might dissolve some aluminium, thereby forming a quaternary kappa-(Hf–Mo–B–Al) phase (*10*). Complete solid solubility between the kappa-phases in the ternary systems Hf–Mo–B and Zr–Mo–B was also found to exist. The kappa-phase reported by Whitehead and Brownlee to have the composition $W_{16}Ni_3C_6$ (*29*) is identical to the kappa-(W–Ni–C) phase listed in Table I and the chemical composition of this kappa-phase is, according, to microprobe measurements, close to W_3NiC (*30*). A quaternary kappa-phase, probably homogeneous over the whole range of Fe/Ni ratios, occurs in the system Fe–Ni–W–C (*35*).

4. Preparation and Properties of Kappa-Phases

The kappa-phases have generally been prepared by high-temperature reaction under vacuum or a protective atmosphere between the constituent elements or suitable combinations of elements and binary compounds. The latter method has been used particularly when one of the com-

TABLE I

TERNARY AND QUATERNARY SYSTEMS CONTAINING KAPPA-PHASES

	Unit cell dimensions			
System	a (Å)	c (Å)	V (Å^3)	References
Hf–Mo–B	8.565	8.493	540	*23, 9*
Zr–Mo–B	8.634	8.566	553	*10*
Hf–W–B	8.592	8.491	543	*23, 9*
Zr–W–B	8.619	8.635	556	*10*
Hf–Re–B	8.456	8.524	528	*11*
Zr–Re–B	8.525	8.651	544	*11*
Hf–Os–B	8.512	8.510	534	*11*
W–Cr–C	7.755	7.764	404	*24*
W–Mn–C	7.756	7.756	404	*2, 25*
W–Fe–C	7.806	7.806	412	*26, 1, 16*
W–Co–C	7.848	7.848	419	*1, 3, 13, 27, 28*
W–Ni–C	7.848	7.848	419	*2, 1, 29, 30*
W–Mn–Al–C	7.903	7.787	421	*7*
Mo–Mn–Al–C	7.876	7.867	423	*7*
W–Fe–Al–C	7.895	7.857	424	*7*
Mo–Fe–Al–C	7.849	7.848	419	*7*
Mo–Co–Al–C	7.950	7.843	429	*7*
Mo–Ni–Al–C	7.893	7.850	424	*7*
Mo–Cu–Al–C	7.952	7.865	431	*7*
Ti–Mn–O	7.8396	7.8776	419.3	*18*
Ti–Fe–O	7.8329	7.8759	418.5	*18*
Hf–Mo–O	8.609	8.536	548	*11*
Zr–Mo–O	8.684	8.449	552	*11*
Hf–W–O	8.595	8.444	540	*11*
Zr–W–O	8.674	8.491	553	*11*
Hf–Re–O	8.535	8.385	529	*11*
Zr–Re–O	8.568	8.498	540	*11*
Hf–Os–O	8.570	8.435	537	*12*
Zr–Os–O	8.613	8.552	562	*12*
Hf–Mo–Si	8.6233	8.5775	552.4	*19, 21*
Hf–Re–Si	8.5643	8.6377	548.7	*20*
Hf–Os–Si	8.6642	8.5157	553.6	*22*
Hf–Mo–P	8.6236	8.6101	554.5	*19, 21*
Hf–W–P	8.6382	8.6367	558.1	*19*
Hf–Re–P	8.5666	8.6221	548.0	*20*
Hf–Os–P	8.6339	8.5460	551.7	*22*
Hf–Mo–S	8.6796	8.5341	556.8	*19, 21*
Hf–W–S	8.6682	8.5627	557.2	*20*
Hf–Re–S	8.5907	8.5008	543.3	*20*
Hf–Os–S	8.6557	8.4754	549.9	*22*
Hf–Mo–Ge	8.6396	8.6827	561.3	*19, 21*
Hf–Re–Ge	8.5771	8.6642	552.0	*20*
Hf–Os–Ge	8.6630	8.5135	553.3	*22*
Hf–Mo–As	8.6559	8.6646	562.2	*19, 21*
Hf–W–As	8.6741	8.6967	566.7	*20*
Hf–Re–As	8.5968	8.6075	550.9	*20*
Hf–Os–As	8.6570	8.4985	551.6	*22*
Hf–Mo–Se	8.6995	8.6234	565.2	*19, 21*
Hf–W–Se	8.7073	8.6674	569.1	*20*
Hf–Re–Se	8.6050	8.5614	549.0	*20*
Hf–Os–Se	8.6540	8.4782	549.9	*22*
Hf–Mo–Fe	8.611	8.411	540	*10*
Zr–Mo–Fe	8.685	8.444	552	*10*
Hf–W–Fe	8.601	8.399	539	*10*
Hf–Re–Fe	8.5830	8.4178	537.0	*20*
Hf–Os–Fe	8.6298	8.4535	545.2	*22*
Hf–Mo–Co	8.632	8.475	547	*10*
Zr–Mo–Co	8.73	8.54	564	*31*
Hf–W–Co	8.628	8.481	547	*10*
Hf–Re–Co	8.6077	8.4281	540.8	*20*
Hf–Os–Co	8.6239	8.4578	544.7	*22*
Hf–Mo–Ni	8.652	8.498	551	*10*
Zr–Mo–Ni	8.748	8.507	564	*10*
Hf–W–Ni	8.645	8.498	550	*10*
Hf–Re–Ni	8.6261	8.4367	543.7	*20*
Hf–Os–Ni	8.6391	8.4766	547.9	*22*
Mn_3Al_{10}	7.543	7.898	389.2	*8*
Co_2Al_5	7.593	7.656	383.3	*4*
Mn_3SiAl_9	7.513	7.745	378.6	*32*
Al–Mn–Si–Zn	7.527	7.818	383.6	*33*
Cu_3Cd_{10}	8.118	8.751	499.4	*34*

Note. The kappa-phase unit cell dimensions are variable, but only one set of characteristic values is given. Consult original references for details on composition and lattice parameter variation.

ponent elements is very volatile (P, As, S, Se) (*19–21*). Binary phosphides, arsenides, etc., have then been synthesized beforehand by the sealed silica tube technique or by other means. In some cases, the kappa-phases are formed directly on solidification from the melt, but normally annealing treatments are necessary for homogenizing the products. The melting or decomposition temperatures for the kappa-phases are generally higher than 1700 K. Solidification studies in the Co–W–C system (*27*) indicate that the kappa-(W–Co–C) phase is stable well above 2000 K. Kappa-(Ti–Fe–O) has been reported as a high-temperature phase, being stable only above approximately 1400 K, with a melting temperature between 1600 and 1700 K (*18*).

The chemical and physical properties of the kappa-phases have been explored very little, and the information is extremely meager. It appears, however, that all kappa-phases are fairly hard, brittle materials exhibiting metallic conductivity. Magnetic ordering has not been detected in any of the kappa-phases. For kappa-(Ti–Fe–O) and kappa-(Ti–Mn–O) temperature-independent paramagnetism has been observed from 80 to 600 K (*18*).

5. Atomic Order and Disorder in the Kappa-Phase Structures

5.1. *The Metal Atom Sublattice*

The ternary kappa-phases contain two transition metal components (M and M') and a third component (X) which can either be a nonmetal or a $3d$ transition metal. The two components M and M', located on the $12k$ position, two $6h$ positions, and the $2a$ position, can be regarded as constituting a metal atom sublattice ("the host lattice") containing various types of interstice. In the ideal kappa-phase structure the two components M and M' are distributed in an ordered manner with M-type atoms on the $12k$ and $6h$(I) positions and M'-type atoms on the $6h$(II) position. For the $2a$ position, two ideal situations can be distinguished. The $2a$ position can either be occupied by M-type atoms (as in $W_{10}Co_3C_{3.4}$ (*13*)) or by M'-type atoms (as in Hf_9Mo_4Ni (*14*)).

Deviations from the ideal compositions of the host lattice have been found to occur quite frequently and are caused by substitutions by M atoms on the M' sites or vice versa. The degree of substitution is often variable, and many kappa-phases accordingly display extended ranges of homogeneity. The kappa-phases in the systems Hf–Mo–{Si, P, S, Ge, As, Se} have been studied in some detail (*21*), and the differences in their maximum and minimum unit cell volumes are presented in Table II. Phase analytical (*21*) and crystallographic (*15, 17*) results indicate that hafnium substitution on the molybdenum $6h$(II) and $2a$ sites is the major cause of the variations in compositions and lattice parameters observed. It has been suggested that the variations in the extensions of the homogeneity ranges are due to the thermodynamic stability of the kappa-phases in relation to the neighboring phases (*21*). An increased relative stability of the kappa-phase would increase the degree of Hf/Mo substitution and hence the width of the homogeneity range, since the tangent point on the free-energy surface of the kappa-phase is shifted toward a larger hafnium content.

TABLE II

THE DIFFERENCES (Δ) BETWEEN THE MAXIMUM AND MINIMUM UNIT CELL VOLUMES OF THE KAPPA-PHASES IN THE TERNARY SYSTEMS Hf–Mo–{Si, P, S, Ge, As, Se} (*21*)

System	Δ ($Å^3$)
Hf–Mo–Si	0.74
Hf–Mo–P	3.67
Hf–Mo–S	14.08
Hf–Mo–Ge	0.16
Hf–Mo–As	1.87
Hf–Mo–Se	2.37

For kappa-(Ti–Fe–O), neutron diffraction data indicate some Fe/Ti substitution on the $2a$ position (*18*), and for kappa-(W–Fe–C), neutron diffraction data indicate Fe/W substitution on both the $6h$(I) and the $2a$ tungsten positions (*16*). These results are in both cases confirmed independently by Mössbauer spectroscopic studies (*18, 36*).

The occurrence of M/M' substitution explains some observations of kappa-phase unit cell volumes, which were considered anomalous before detailed structural information became available. This was for instance the case of the two kappa-carbides kappa-(W–Fe–C) and kappa-(W–Co–C), where the iron carbide has a smaller cell volume than the cobalt carbide in spite of the fact that the iron metal atom radius is larger than that of cobalt. Neutron diffraction data show that the atomic distribution is almost ideal in the cobalt carbide metal sublattice (*13*) while, as mentioned above, a considerable number of the larger tungsten atoms are replaced by the smaller iron atoms in the iron carbide (*16*). An analogous situation exists for the osmium- and rhenium-containing kappa-phases, where the osmium phases invariably have larger unit cells than the corresponding rhenium phases (see Table I), although the rhenium radius is larger than that of osmium. Presumably a greater degree of Hf/Os substitution than Hf/Re substitution in the corresponding kappa-phases is responsible for this effect.

5.2. *The Filling of the Interstices*

The metal atom host lattice of the kappa-phases contains a large number of interstices. The most important of them are shown in Fig. 2, where three types of sites are indicated: the octahedral 6*g* sites, the octahedral 4*f* sites, and the trigonal–prismatic 2*c* sites. In addition to these voids the host lattice contains square–pyramidal interstices (situated outside the quadrilateral faces of the trigonal prisms) and tetrahedral interstices. The latter are not included in Fig. 2, but they can be distinguished in Fig. 1 as situated both inside the icosahedra and between the icosahedra and the surrounding octahedra. With the exception of the tetrahedral interstices all interstices are exclusively surrounded by *M*-type atoms in the ideal kappa-phase structure.

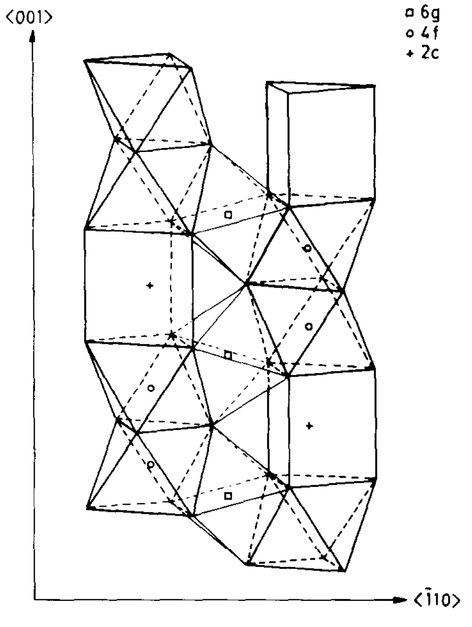

FIG. 2. Part of the kappa-phase structure projected along a direction almost perpendicular to the (110) plane. The positions of the interstices have only been marked in one unit cell. All corners of the polyhedra represent atomic positions 12*k* and 6*h*(*I*).

Ordinarily, only two types of interstice, the octahedral 6*g* and the trigonal–prismatic 2*c* sites, are occupied. It has been found, however, that hydrogen can be dissolved interstitially in some kappa-phases (*22, 37*), and it seems obvious that the hydrogen atoms must occupy other interstices as well.

The size of the trigonal–prismatic interstices is always larger than that of the 6*g* octahedral interstices. A typical radius difference between the two voids is about 0.4 Å for a hafnium-containing kappa-phase. Only atoms with the smallest radii (O, C, S) might be expected to occupy the octahedral sites. Table III indicates the various modes of filling the 2*c* and 6*g* interstices in ternary kappa-phases.

X-ray single-crystal structure refinements of the kappa-phases in the ternary systems Hf–Mo–B (*10*), Hf–Mo–Ni (*14*), Hf–Mo–P (*15*), and Hf–Mo–Se (*17*) have established that the elements B, Ni, P, and Se enter the 2*c* position of the host lattice. None of the investigations indicated any vacancy formation on this site. It seems reasonable to assume an identical situation to prevail also for other kappa-phases containing B, Ni, P, and Se. The kappa-phases containing the elements Fe, Co, Si, As, and Ge as the *X* component are expected to belong to this class too, since the radii of

TABLE III

THE VARIOUS MODES OF FILLING THE TWO TYPES OF INTERSTICES IN THE KAPPA-PHASES IN THE TERNARY SYSTEMS M–M'–X

X	Sites occupied 2c	 6g
O		x
C	x	x
S	x	x
B, Si, P, Ge, As, Se	x	
Fe, Co, Ni	x	

Note. M and M' are the two transition metal components constituting the host lattice and X denotes the elements filling the interstices.

these elements are too large to be accommodated in the octahedral site.

The only kappa-phases for which the octahedral 6g site has been reported to be occupied exclusively are the kappa-oxides (*11, 12, 18*). Observed variations in unit cell volume for the kappa-(Zr–Mo–O) phase (*11*) indicated a small range of homogeneity, which was proposed to be due to a variable amount of vacancies on the 6g oxygen site.

A simultaneous occupation of both 2c and 6g interstices has been found to occur in the kappa-carbides (*13, 16*). The 2c position was found to be occupied only to a fractional degree, leaving some 50% of the sites vacant. Both interstices are also occupied in the quaternary kappa-(Hf–Mo–Ge–O) phase, with germanium atoms on the 2c site and oxygen on the 6g site, but vacancy formation was here found to occur on both positions (*17*). For the kappa-phase in the Hf–Mo–S system, the phase analytical results indicate sulfur contents in excess of those corresponding to the filling of the 2c position. It is therefore most probable that the 6g sites are filled with sulfur to some 6–9% (*21*).

6. Concluding Remarks

Nowotny and co-workers have earlier touched upon various aspects of the kappa-phase crystal chemistry in several review articles (*38–44*). For instance, considerations have been made of the stabilizing effect of aluminium (*38, 40*), the structural relationship to the tungsten bronzes (*41*), the octahedral network (*38, 40–42*), and the combination of octahedral and trigonal–prismatic interstices (*44*).

From the space-filling point of view, the exclusive filling of only octahedral 6g or only trigonal–prismatic 2c interstices in the kappa-phase metal host lattice is less efficient. Nevertheless, the great majority of the ternary kappa-phases belongs to one of the two categories, most of them, in fact, to the trigonal–prismatic type although this leaves the largest number of interstices empty. It seems reasonable to connect this observation with the size factor, the size of the octahedral holes being much smaller than those of the trigonal–prismatic ones.

It would, for instance, be inconceivable that the 3d elements Fe, Co, and Ni should enter the octahedral holes, and even the trigonal–prismatic positions appear very small. The six hafnium nearest-neighbors of nickel in kappa-(Hf–Mo–Ni) are indeed at very short distances: 2.57 Å (*14*). However, there are also three additional hafnium neighbors at a distance exceeding the Goldschmidt metal radius sum by only 10%, providing a three-capped trigonal–prismatic nine-coordination, which is very common with iron group metals in intermetallic compounds with metals of large radii (particularly the rare-earth metals).

The conditions for a simultaneous occupation of both octahedral and trigonal–prismatic voids should be more favorable for those p elements having the smallest radii (O, N, C, B, S, P). Regarding oxygen and nitrogen there is no structure known where these elements take a trigonal–prismatic transition metal coordination. In contrast, boron favors trigonal–prismatic coordination almost exclusively. For phosphorus, the TiP structure (*45*) provides an example where both octahedral and trigonal–prismatic interstices are occupied, but there is no evidence for an analogous situation in kappa-(Hf–Mo–P) (*15*). For sulfur, however, there is strong evidence for a partial occupation of the octahedral sites, together with full occupation of the trigonal–prismatic sites in kappa-(Hf–Mo–S) (*21*), and in the case of the kappa-carbides, carbon occupation of both types of interstice has been definitively established by neutron diffraction measurements (*13, 16*).

In quaternary systems containing two different *p* elements, these might fill both the octahedral and the trigonal–prismatic holes in an ordered fashion. One such example is the quaternary Hf–Mo–Ge–O kappa-phase, with partial occupation by oxygen of 6*g* and germanium of 2*c* (*17*). Another example is kappa-(Hf–Mo–Ni), where the structure refinement indicated some occupancy of 6*g*, most probably by oxygen (*14*).

There is some indirect evidence that the simultaneous occupation of the two types of interstitial site is connected with an enhanced thermodynamic stability. The very large homogeneity range of kappa-(Hf–Mo–S) as compared with other kappa-(Hf–Mo–X)-phases gives support to this idea (*21*), and the ease with which quaternary kappa-(Hf–Mo–Ge–O) is formed in contrast to ternary kappa-(Hf–Mo–Ge) is a further argument in favor of the hypothesis.

A conspicuous feature of Table I is the total absence of nitrogen-containing phases. One would expect such phases to be analogous to the kappa-oxides (nitrogen strongly preferring octahedral metal coordination like oxygen), but attempts to prepare kappa-nitrides have so far been unsuccessful. If the hypothesis of a simultaneous 6*g*/2*c* occupation giving an increased thermodynamic stability is correct, there is a possibility that quaternary kappa-nitrides can be synthesized, in analogy to kappa-(Hf–Mo–Ge–O).

It was mentioned previously that hydrogen can be dissolved interstitially in kappa-phases. From the crystal chemical principles that seem to govern hydrogen absorption in transition element/*p* element compounds (*46*), it can be concluded that all titanium-, zirconium-, and hafnium-containing kappa-phases should be capable of dissolving hydrogen. Depending on the *p* element distribution on 6*g* and 2*c*, different conditions prevail for the hydrogen atom locations, since hydrogen atoms tend to avoid *p*-element atoms as far as possible (*46*). It is therefore anticipated that at least part of the hydrogen atoms dissolved in kappa-(Ti–Fe–O) (*37*), with oxygen exclusively on 6*g*, take positions which are different from those in kappa-(Hf–Mo–P) (*22*), with phosphorus exclusively on 2*c*.

Regarding the transition metal constituents in the kappa-phases, the great abundance of hafnium-containing compounds is noteworthy (see Table I). There are only a few phases containing zirconium instead of hafnium, although these two metals are very similar in both atomic size and chemical behavior.

Aluminum evidently behaves in a different way compared with other *p* elements, since it undoubtedly occupies positions within the metal host lattice (*7*).

In concluding the present survey one might remark that although no reliable criterion for predicting the existence or nonexistence of new kappa-phases has yet been found, the kappa-phase research has brought forward a great deal of interesting structural information. For instance, the kappa-phases most probably provide the only example of isomorphism between a transition metal silicide and a selenide. In fact, the kappa-phase structure is an almost unique case in crystal chemistry by virtue of its capacity of accommodating so many different p elements within the same basic metallic framework.

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