

Structural relationships between cations and alloys; an equivalence between oxidation and pressure

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More than 100 examples are provided of the structural identity between the cation arrays in oxides and their corresponding alloys (binary compounds). Halides and halogenates, sulfides and sulfites and/or sulfates, selenides and selenates, phosphides and phosphates show this behaviour. In some cases, the structure of the cation subarray corresponds to the structure of the alloy at ambient conditions, but in other cases, cations stabilize structures which correspond to those of the high-pressure phases of the alloy, from which an analogy between the insertion of oxygen and the application of pressure can be established. In this last case, the oxides show polymorphism with temperature and when heated, the structure of the ambient pressure of the alloy is recovered as if heating would compensate the effect of pressure. From the results reported here, it is concluded that cations do not seem to be either the isolated entities, predicted by the ionic model, which occupy interstices of an oxygen matrix, or they arrange in a more or less arbitrary way, but they try to reproduce the structure of their corresponding alloy. Many of the phase transitions and the polymorphism exhibited by the oxides described here are better explained when they are considered as formed by previous entities which are the alloys. Oxides should be considered as 'real stuffed alloys'. These features do not seem to be casual, but they obey a general principle: Cations recognize themselves in spite of being embedded in an oxygen bulk. The nature and the physical meaning of this recognition are problems which remain unsolved.

1. Introduction

The most common approach for describing and classifying crystal structures of extended inorganic solids starts from the short-range order, *i.e.* the coordination numbers and coordination polyhedra exhibited by the constituting elements which are rationalized by considering ratios of radii or specific electron configurations of the respective central atoms. The full three-dimensional crystal structures are communicated by giving the connectivity of the coordination polyhedra. This approach suffers from various drawbacks. Among these are the arbitrariness in defining the coordination spheres and the lack of any tool for systematically classifying the long-range order. The latter point is particularly serious since, in extended inorganic solids, in contrast to molecular solids, long-range bonding interactions play an important role, determining physical and structural properties. The situation is even more dramatic when trying to describe structures in a simple, easy and comprehensible way. An example of such a situation is the structure of apatite, which cannot be understood at all in terms

Table 1

Structures of the alkali halides together with the structures formed by the cation arrays in their oxides.

HP are high-pressure phases, LT are low-temperature phases, TL is a phase stable in thin layers and B-r is a phase related to Blende.

Halides	Structure types	Oxides	Cation arrays
LiCl	B1	None	
NaCl	B1, B2 (HP)	NaClO ₂ /NaClO ₃ /NaClO ₄	NaCl(d)/NaCl(d)/NaCl
KCl	B1, B2 (HP)	KClO ₃ /KClO ₄	CrB, NaCl, CsCl/FeB, NaCl
RbCl	B1, B2 (HP)	RbClO ₃ /RbClO ₄	CsCl/FeB, NaCl
CsCl	B1 (LT), B2	CsClO ₄	FeB, NaCl
LiBr	B1	None	
NaBr	B1, CrB (HP)	NaBrO ₃	NaCl(d)
KBr	B1, B2 (HP)	KBrO ₃ /KBrO ₄	CsCl/FeB
RbBr	B1, B2 (HP)	RbBrO ₃	CsCl
CsBr	B1 (LT), B2	CsBrO ₃ /CsBrO ₄	CsCl/Scheelite
LiI	B1	LiIO ₃ /LiIO ₄	NaCl (d)/anti-FeB, B-r
NaI	B1, CrB (HP)	NaIO ₃ /NaIO ₄	CsCl/Scheelite
KI	B1, B2 (HP)	KIO ₃ /KIO ₄	CsCl/Scheelite
RbI	B1, B2 (HP)	RbIO ₃ /RbIO ₄	CsCl/Scheelite
CsI	B1(LT), B2, TL	CsIO ₃ /CsIO ₄	CsCl/Scheelite

of cation-centered anion polyhedra. This has led O'Keeffe & Hyde (1985) to propose an alternative model, based on the cation arrays, which describes the structures of oxides as oxygen-stuffed alloys. On the other hand, it has been reported (Martínez-Cruz *et al.*, 1994) that the oxidation process of an alloy could be regarded as an equivalent to the application of pressure. This idea was stimulated by the publication of the CrB → CsCl transition, under pressure, in the BaSn alloy (Beck & Lederer, 1993). It is well known that the CsCl structure is that adopted by cations in the cubic ABO₃ perovskites, one of these being the BaSnO₃ oxide. Thus, oxidation and pressure had produced the same structural effect on the BaSn array. Amazingly, the unit-cell volumes of both the high-pressure and 'oxidized' phases were virtually the same as if the three O atoms would have been inserted without any volume increase. This led the authors to establish the concept of a 'real stuffed alloy' for those oxides whose cation arrays maintained the structure of the corresponding alloy (Martínez-Cruz *et al.*, 1994).

This concept seems to offer the opportunity to have a more physical meaning than the model proposed by O'Keeffe & Hyde (1985), regarding oxides as oxygen-stuffed alloys but where the cation arrays do not necessarily coincide with the structure of the corresponding element or alloy. Only in four instances, reported therein, was this coincidence evident. These were HT-NaClO₄ and HT-BaSO₄ (where HT represents high-temperature), and Ca₂SiO₄ and Y₅Si₃O₁₂N, which also behave as 'real stuffed alloys'. It should be pointed out that the O'Keeffe & Hyde model had only a descriptive purpose and that for this reason, the four examples cited above were considered as 'striking features'.

Further, new examples of such compounds were reported as in the case of the (RE)AlO₃ perovskites (Ramos-Gallardo &

Vegas, 1997) and the oxides Rb₃BiO₃ and Cs₃BiO₃ (Zocher & Jansen, 1997a,b).

It has been suggested elsewhere (Vegas, 2000) that the validity of the concept of 'real stuffed alloys' could be extended considerably and thus generalized, if the cation arrays, in oxides, are regarded as metastable structures of the corresponding alloy. This is the case of the recently reported study of Na₂S under pressure (Vegas *et al.*, 2001) in which an Ni₂In-type phase of Na₂S is obtained at 7.6 GPa. This phase has the same structure as the cation arrays of three high-temperature phases of the corresponding oxide Na₂SO₄.

Although other similar studies are actually in progress, we report here a wide, but not at all exhaustive, search of real stuffed alloys with a double purpose. On one hand to see how general is the appearance of this phenomenon, which eventually could be formulated as a 'general principle'. On the other hand to obtain new examples for the equivalence of oxidation and pressure, which could help us to understand and classify the crystal structures of oxides.

In this work, the term alloy will denote any binary compound which gives rise to a given oxide. Hence, it also comprises ionic compounds as the alkali halides.

2. Description of the structures

2.1. Alkali halides and halogenates

All the alkali halides AX (*A* = Li, Na, K, Rb, Cs; *X* = Cl, Br, I) present the NaCl (*B1*) structure at room temperature and pressure with the exception of CsCl, CsBr and CsI, which are stable at low temperature. These last three compounds have the CsCl (*B2*) structure under normal conditions and many others such as ACl (*A* = Na, K, Rb, Cs), ABr (*A* = K, Rb, Cs) and AI (*A* = K, Rb, Cs) undergo the *B1* → *B2* transition under pressure. This transition has not been observed in NaBr and NaI which, instead, undergo the transition *B1* → TII (CrB) at high pressures (Leger *et al.*, 1998). The compounds are listed in Table 1 together with their respective ternary oxides.

2.2. Chlorates

No lithium chlorate has been reported. Three sodium chlorates are known, *i.e.* NaClO₂, NaClO₃ and NaClO₄. In all of them, the NaCl subarrays correspond to a distorted NaCl type. NaClO₄ is isostructural with anhydrite (CaSO₄) and transforms at 581 K to a cubic phase where the Na and Cl atoms have the positions of NaCl itself. This can be interpreted as if the insertion of two, three or four O atoms would exert an internal pressure which is not sufficient to produce the *B1* → *B2* transition (which occurs at 17.6 kbar), but high enough to distort its structure. When this pressure is compensated by increasing the temperature, the cubic array of NaCl is recovered, as has been demonstrated experimentally for NaClO₄.

Two potassium salts are known, KClO₃ and KClO₄. The former has three phases. At ambient conditions it is monoclinic (*P*₂/*m*) and its KCl subarray is of the CrB type (O'Keeffe & Hyde, 1985), where each atom is coordinated by

seven unlike atoms. At high temperature there is a transition to orthorhombic ($Pnma$), where the coordination number remains as 7, but where blocks of the NaCl structure appear. At high pressures (> 6 kbar), the monoclinic structure transforms to rhombohedral ($\alpha = 85.2^\circ$) with a cation partial structure resembling the CsCl-type structure, which is adopted by the HP phase of KCl. $KClO_4$ is orthorhombic at ambient conditions. The cations, as in barite ($BaSO_4$), have the FeB structure with coordination number 7. At 513 K, the barite-like structure transforms to cubic ($F\bar{4}3m$) with the cations arranged as in NaCl. Again, the two phases of KCl appear in the related ternary oxides. The insertion of oxygen produces an internal pressure which increases the CN from 6 to 7 in both the CrB- and FeB-type structures. When the effect of pressure is compensated by increasing the temperature, the NaCl-type structure is recovered in both oxides. It is worthwhile mentioning that $KClO_3$ transforms to a CsCl-type array by applying a relatively small pressure of 6 kbar. In this case, the cations (K and Cl) undergo the CrB \rightarrow CsCl, transition in spite of being embedded in an oxygen matrix.

The rubidium salts $RbClO_3$ and $RbClO_4$ have a similar behaviour. Under normal conditions $RbClO_3$ adopts the rhombohedral distortion of the CsCl structure ($\alpha = 86.42^\circ$). $RbClO_4$ also has the barite-type structure, but at high temperature it undergoes a transition to a cubic phase with cations arranged as in NaCl. Here again, the two phases of RbCl appear in the corresponding oxides.

$CsClO_4$ is the only caesium salt reported. Its cation array is also of the FeB type, which transforms at high temperature to the cubic phase where cations recover the NaCl-type structure of CsCl.

2.3. Bromates

The oxides derived from A Br behave in the same manner as the chlorates. $NaBrO_3$ has a unique cubic phase ($P2_13$), where the Na^+ and Br^{5+} cations adopt a distorted NaCl structure as in NaBr itself.

$KBrO_3$ has a rhombohedral structure ($\alpha = 85.96^\circ$), which can be regarded as a distortion of the cubic perovskite with cations in CsCl structure, reproducing the high-pressure phase of KBr. $KBrO_4$ belongs to the barite group. Although no high-temperature study has been reported it is expected to show a behaviour similar to that of $RbClO_4$, transforming at high temperature in the cubic phase with the NaCl structure.

$RbBrO_3$ also crystallizes in the rhombohedrally distorted perovskite ($\alpha = 87.6^\circ$), reproducing the CsCl-type array of RbBr itself. $RbBrO_4$ is still unknown.

$CsBrO_3$ has a distorted perovskite-like structure ($\alpha = 88.7^\circ$), which reproduces the CsCl-type structure of CsBr. $CsBrO_4$ is not barite-like. Instead, it adopts the scheelite structure. In scheelite, both cations form a tetragonally distorted *f.c.c.* (face-centered cubic) array in which the 4^4 planar nets are formed by alternate A and B cations, which corresponds to the (002) planes of the NaCl structure. In the latter, these 4^4 nets are stacked in the ..*ABAB*.. sequence, whereas in scheelite they are stacked in the ...*ABCDABCD*... sequence. As a result

each A cation (Cs in our case) is coordinated by eight Br atoms and at the same distances by four additional A atoms, producing the total CN = 12 of a *f.c.c.* array. It would be interesting to know whether at high temperatures the scheelite-like structure transforms into a cubic phase with a NaCl-like array as it occurs with the compounds of the barite group. As far as we know, no such study has been reported.

2.4. Iodates

Three phases of $LiIO_3$ have been described. At room temperature, the structure is hexagonal ($P6_3$), in which the LiI subarray is a distorted NiAs type. The *h.c.p.* (hexagonal close packing) array is formed by the I atoms and the Li atoms occupy all the octahedral holes. However, they are not located at the center of the octahedra, but shifted towards one of the triangular faces, giving rise to a CN of $3 + 3$. At 488 K, this phase transforms to an orthorhombic phase which is of the *anti*-FeB type, in which the Li atoms are inserted into the trigonal prisms formed by the I atoms. At 513 K a second phase transition transforms $LiIO_3$ into a tetragonal phase, where the LiI subarray form a very distorted NaCl-type structure. Although the distortion is very strong, the structure of LiI itself can clearly be identified in the oxide. The existence of the *anti*-NiAs structure cannot be justified within this model, but the *anti*-FeB phase behaves as the other compounds of the barite group, that is, when temperature increases the low pressure phase (NaCl, even distorted) is attained.

$NaIO_3$ is orthorhombic ($Pbnm$). Here, the Na^+ and I^{5+} cations form a structure of the CsCl-type. As mentioned previously, this phase is lacking for NaBr and NaI. Instead a TII (CrB) derivative has been reported at high pressures (Leger *et al.*, 1998). Owing to the pressure-induced CrB \rightarrow CsCl transition, it is to be expected that at higher pressures the CsCl structure can be isolated. $NaIO_4$ presents the scheelite structure. Its relationship with the NaCl-type phase of NaI has been discussed above.

Potassium, rubidium and caesium iodates behave in the same manner. All three form the compounds AIO_3 and AIO_4 ($A = K, Rb, Cs$). AIO_3 crystallizes in the perovskite analog. They are rhombohedrally distorted for the K and Rb compounds (α angles of 89.2 and 89.7° , respectively) and cubic ($Pm\bar{3}m$) for $CsIO_3$. In all three compounds, the insertion of oxygen stabilizes the CsCl-type phase of the halides (high-pressure phases in the case of KI and RbI). The three AIO_4 compounds are scheelite-like and, as said above, they are related to the NaCl-type structure of the halides. Nevertheless, in the case of $CsIO_4$ there is an additional relationship which should be briefly discussed. It has been reported that CsI crystallizes, in thin layers and at 133 K, in a tetragonal structure ($P\bar{4}b2$; Morlin, 1971), which is directly related to the cation array in scheelite. Both, the cation array in scheelite and the tetragonal phase of CsI are represented in Figs. 1 and 2, respectively. It consists of (001) NaCl layers, perpendicular to a , which are displaced by $(a/4 + c/4)$ with respect to each other, as in scheelite (remember that these layers are

Table 2

Compounds ABO_4 of the $CrVO_4$ type, whose AB subarrays are of the NiAs-type.

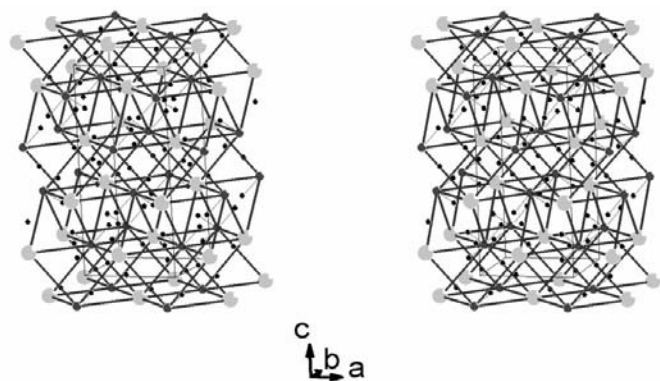
In the last column the structures of the AB binary alloys are listed.

Compound	Alloy	Structure type
β - $CrAsO_4$	AsCr	NiAs, MnP
$CdSO_4$	CdS	Wurtzite, NaCl, CrN
$CoCrO_4$	CoCr	CrFe
$CoSO_4$	CoS	NiAs
$CoSeO_4$	CoSe	NiAs
$CrCuO_4$	CrCu	Not found
$CrMgO_4$	CrMg	Not investigated
$CrNiO_4$	CrNi	Cu
$CrPO_4$	CrP	MnP
$CrVO_4$	CrV	W
$CuSO_4$	CuS	CuS
$FeSO_4$	FeS	NiAs, MnP
$InPO_4$	InP	Blende \rightarrow NaCl \rightarrow β -tin
$InVO_4$	InV	Not found
$LiMnO_4$	LiMn	Not found
$MgSO_4$	MgS	NaCl (MgPo as NiAs)
$MnSO_4$	MnS	Blende \rightarrow NaCl
$MnSeO_4$	MnSe	NiAs (HP)
$NiSO_4$	NiS	NiAs (LT)
$NiSeO_4$	NiSe	NiAs
$TiPO_4$	TiP	AsTi (NiAs-related), $CrTiP_2$ as NiAs
$TiPO_4$	TiP	Not investigated
VPO_4	PV	NiAs
$ZnSO_4$	ZnS	Blende \rightarrow NaCl

displaced by $a/2$ in NaCl). The difference is that they are stacked in an $\dots ABAB\dots$ sequence in the alloy, whereas they are stacked in the $\dots ABCD\dots$ sequence in the scheelite-like oxides. Thus, a structure which is very close to a metastable phase of CsI has been stabilized in the oxide in such a way that the cation array in scheelite has no longer to be regarded as a strange structure for the alkali halides.

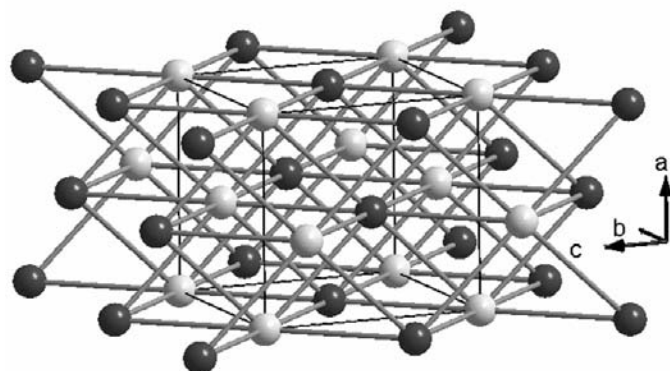
2.5. Compounds ABO_4 of the $CrVO_4$ type

Table 2 lists all the compounds having the $CrVO_4$ structure. All are orthorhombic and crystallize in the space groups $Cmcm$ or $Pnma$. Some are dimorphous and only one ($CoSO_4$) realises an additional monoclinic phase ($P2_1/m$). Dunitz & Pauling(1965) was the first who observed that in the three

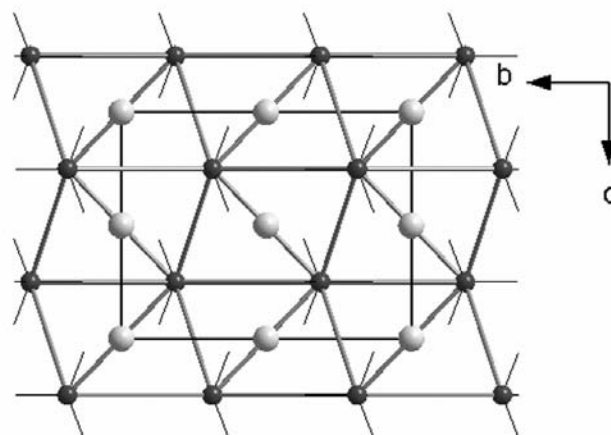

Figure 1

Stereopair showing the scheelite-like structure of $CsIO_4$. Large white atoms represent Cs atoms; medium-sized black circles I atoms; small black circles O atoms.

phases of $CoSO_4$, the cation array is almost identical and that its structure is of the NiAs-type, where the S atoms form a *h.c.p.* array and the Co atoms occupy all the octahedral holes. An alternative description of the structure is based on a simple hexagonal array of Co atoms with alternate trigonal prisms occupied by SO_4^{2-} anions. The structure is represented in Fig. 3. In Table 2 the corresponding binary alloys and the structures adopted by them are listed. They will be compared with the NiAs type present in the oxides. In five cases ($CrCu$, $CrMg$, InV , $LiMn$ and PTi) this comparison is impossible, because the corresponding alloy either has not been investigated or has not been found under the experimental conditions used. Four further representatives ($CoCr$, $CrNi$, CrV and CuS) have structures which are not related to the NiAs-type. However, in the remaining majority the structure of the alloy is either NiAs itself or corresponds to the *f.c.c.* analog, which is the NaCl structure. It cannot be casual that ten of these 24 oxides reproduce the NiAs (or the distorted MnP) structure of their corresponding alloy. In the case of PTi , the NiAs structure has not been observed so far. Instead, the alloy adopts the AsTi-type structure which is midway between NaCl and NiAs. It is


Figure 2

The structure of the tetragonal phase of CsI . Grey circles represent Cs atoms and black circles I atoms. To be compared with Fig. 1.


Figure 3

The cation array of $MgSO_4$, which adopts the NiAs structure type.

Table 3
Chalcogenides of divalent metals and their respective oxides.

In the last column the structures of the cation arrays are listed.

Alloy	Structure type	Oxides	Cation array
MgS	NaCl	MgSO ₄	NiAs
CaS	NaCl, CsCl	CaSO ₄	Anhidrite, NaCl
SrS	NaCl, CsCl	SrSO ₄	FeB, NaCl
BaS	NaCl	BaSO ₄	FeB, NaCl
PbS	NaCl	PbSO ₃ /PbSO ₄	FeB
ZnS	Blende, Wurtzite, NaCl	ZnSO ₄	Blende, NiAs
CdS	Wurtzite, CrN, NaCl	CdSO ₃ /CdSO ₄	NaCl-rel./NiAs
HgS	Blende, Cinnabar, NaCl	HgSO ₄	Dist.-NaCl
MgSe	NaCl	MgSeO ₃ /MgSeO ₄	Dist.-NaCl/unknown
CaSe	NaCl	None	
SrSe	NaCl	SrSeO ₄	Monazite
BaSe	NaCl	BaSeO ₃	Dist.-NaCl
PbSe	NaCl, CsCl	PbSeO ₄	Monazite
ZnSe	Blende, Cinnabar, NaCl	ZnSeO ₃	Dist.-NaCl
CdSe	Wurtzite, NaCl	CsSeO ₃	CsCl
HgSe	Blende, Cinnabar, NaCl	HgSeO ₃ /HgSeO ₄	CsCl/unknown

constituted by pairs of layers of the NiAs type. These pairs of layers are shifted with respect to each other as in NaCl.

With respect to the alloys which adopt the NaCl structure, it should be pointed out that, with the exception of MgS, all of them (CdS, InP, MnS and ZnS) are high-pressure phases. Under ambient conditions they have the blende/wurtzite structure and their respective oxides are further examples of how oxidation and pressure seem to produce the same effect.

2.6. Sulfides and selenides of divalent metals

2.6.1. Sulfides. The compounds which will be discussed in this section are collected in Table 3. They are the sulfides and selenides of alkaline earth metals, and of Zn, Cd, Hg and Pb and the corresponding ternary oxides. The alkaline earth sulfides and PbS crystallize in the NaCl-type structure. For two of them, CaS (Luo *et al.*, 1994) and SrS (Syassen, 1985), an additional HP phase with the CsCl-type structure has been reported. The only corresponding oxides are sulfates MSO₄.

MgSO₄ presents two phases (α and β), stable at room and at high temperature, respectively. Both crystallize in the CrVO₄-type structure and as said in the above section, their cation array is of the NiAs type. Here, cations do not reproduce the NaCl structure of MgS, but instead the *h.c.p.* analog is stabilized.

CaSO₄ is the aristotype of the anhidrite family and its CaS subarray is a distorted NaCl type. As discussed above, for NaClO₄ the insertion of oxygen produces the distortion of the regular NaCl structure, but at 1473 K the anhidrite transforms to a cubic phase where cations form the regular NaCl structure (Pistorius *et al.*, 1969). Again, at high temperatures the effect of pressure is removed and the ambient pressure array of the alloy is obtained.

SrSO₄ and BaSO₄ behave in the same manner. Both are barite-like and, as said above, have a cation array of the FeB-type (CN 7). However, at high temperatures both compounds transform to a cubic phase with the rocksalt structure, with just the array of the corresponding alloys at room pressure.

Two oxides derived from PbS are known, PbSO₃ and PbSO₄. The former presents a rather complicated PbS subarray. It can be described as graphite-like layers in which the six-membered rings are composed of alternating Pb and S atoms. Each atom has additional contacts with atoms of adjacent layers up to complete a CN of 7. The NaCl structure of the alloy is lost here, but yet, rocksalt blocks are recognizable. PbSO₄ belongs to the barite group with the FeB type. Although no high-temperature study has been reported, it is quite possible that it behaves as BaSO₄, transforming into the cubic phase with NaCl structure.

The group 12 sulfides have the blende/wurtzite structure at ambient conditions with HgS the cinnabar structure in addition. At high pressures all of them transform to the NaCl structure. With regards to the oxides, probably the most interesting compound is ZnSO₄, which is isostructural with CrVO₄ and shows a cation array of the NiAs type. That is, the insertion of oxygen stabilizes the *h.c.p.* analog of the NaCl structure, the high-pressure phase of ZnS. At high temperatures (973 K) ZnSO₄ transforms to a cubic phase with the high-cristobalite structure (Spiess & Gruehn, 1978) in which the ZnS subarray has the blende structure. This is another example for recovering the ambient pressure phase of the alloy when pressure is compensated by heating.

Two Cd-containing oxides are known, *i.e.* CdSO₃ and CdSO₄. For the former, three polymorphs have been reported. Two of them are monoclinic ($P2_1/c$) and the third one is trigonal ($R\bar{3}$). In all of them, the cation array is rather irregular. Nevertheless, blocks or elements of the NaCl-type structure can be identified. Thus, the internal pressure produced by the O atoms modifies the wurtzite structure of the alloy, but appears not to be high enough to stabilize the high-pressure phase of CdS (NaCl type). One of the monoclinic polymorphs is particularly interesting since fragments of both the wurtzite and the NaCl structures coexist. These oxides would be good candidates for high-pressure and high-temperature studies. Probably, at high temperature, a wurtzite-like array could be formed and at high pressures the NaCl array would appear.

CdSO₄ has three orthorhombic polymorphs ($Pnma$, $Pn2_1m$ and $Cmcm$). The former is isostructural with CrVO₄ and its cation array is of the NiAs type. In the second one the insertion of oxygen produces a NaCl-type array, which is the high-pressure phase of CdS. In the latter, twinned blocks of a NaCl-type array can be identified. In these oxides, it seems that the insertion of three oxygen atoms per CdS formula unit is not sufficient to produce the HP topologies of the alloy, while insertion of four O atoms clearly stabilizes both the NaCl-type structure and its *h.c.p.* analog, the NiAs structure.

The only oxide derived from HgS is HgSO₄. It has two polymorphs, orthorhombic ($Pn2_1m$) and monoclinic (Pn). The former is isostructural with one of the CdSO₄ phases. In both cases, the cation arrays form a distorted NaCl structure, which correspond to the HP phase of HgS.

2.6.2. Selenides. The selenides and derived oxides (selenites and selenates) are also collected in Table 3. The alkaline earth selenides crystallize in the NaCl structure. For CaSe no

Table 4

ABO_3 compounds whose AB subarrays have either the CrB or the CsCl-type structures.

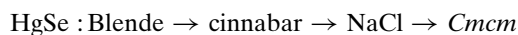
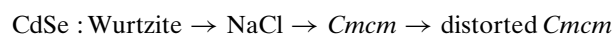
The latter are perovskites.

ABO_3 oxides	AB cation arrays	Structure of the AB alloys
AuLaO ₃	CrB	CrB
BaSiO ₃	CrB	CrB
BaGeO ₃	CrB	CrB
BaSnO ₃	CsCl	CrB, CsCl
AlScO ₃	CsCl	CrB, CsCl
AlYO ₃	CsCl	CrB, CsCl
AlLaO ₃	CsCl	AlCe, CsCl
AlCeO ₃	CsCl	AlCe, CsCl
AlPrO ₃	CsCl	AlDy, AlCe, CsCl
AlNdO ₃	CsCl	AlDy
AlSmO ₃	CsCl	AlDy, CsCl
InYO ₃	CsCl	CsCl
InLaO ₃	CsCl	CsCl
InNdO ₃	CsCl	Possibly CsCl

derived oxide has been reported. SrSeO₄ crystallizes in the monazite-like structure and it will be described in more detail below. BaSeO₃ has a cation array of the NaCl-type, just as BaSe itself.

SrSeO₄ and PbSeO₄ are monazite-like. The structure is represented in Fig. 13 and will be discussed in more detail when the rare earth phosphates will be considered. The cation array in monazite is a strongly distorted NaCl structure in which each Pb(Se) atom is coordinated by seven unlike atoms. It is quite probable that, at high temperature, the structure could transform to another phase with a less distorted, or even regular, array of the cation sublattice with the NaCl structure, as occurs with SrSO₄.

The II–VI selenides exhibit the following transition sequence under pressure (Nelmes & McMahon, 1998)



The corresponding oxides show a different behaviour. ZnSeO₃ has two orthorhombic polymorphs (*Pnma* and *Pcab*). In both, the ZnSe subarray has a distorted NaCl-type structure. That is, the insertion of oxygen stabilizes the high-pressure phase of the alloy. The other two selenites, CdSeO₃ and HgSeO₃, adopt a CsCl-type structure, a phase which could well appear at higher pressures in the corresponding alloys. In fact, HgTe has been reported to have a phase transition from *Cmcm* to a phase V with a possibly distorted CsCl structure (Hu, 1987).

2.7. ABO_3 compounds and the CrB \rightarrow CsCl transition

The compounds considered in this section are collected in Table 4. The first three compounds have their cations arranged

in the CrB-type structure, which is just the structure of their corresponding alloys AuLa, BaGe and BaSi.

The remaining compounds are all perovskites which, as mentioned previously, present a cation array of the CsCl type. Two of these perovskites, LaAlO₃ and NdAlO₃, show rhombohedral distortions with α very close to 90°. The remaining ones are GdFeO₃-type variants. It should be noted that two of these perovskites, ScAlO₃ and YAlO₃, are not stable at ambient conditions, but they are stabilized under pressure. In correspondence with the model of ‘real stuffed alloys’, all of them show a more or less distorted array of the CsCl-type. Only for two alloys (AlNd and InNd) has the CsCl structure not been reported, but the fact that the corresponding members of Pr and Sm exist with this structure leads us to assume that these systems have not been sufficiently explored.

The two structures under consideration for the alloys in Table 4, are in some way related. AlSc and AlY are dimorphous, presenting the two structure types and BaSn, which is a CrB type at ambient conditions, and transforms to CsCl at 3.5 GPa (Beck & Lederer, 1993). In the remaining Al(RE) alloys the stable form is either the AlCe or the AlDy type, the CsCl-type phase being a metastable structure, as has been suggested by Schob & Parthé (1965). In fact, AlLa (CsCl) is only obtained by ultra-rapid quenching from the liquid state (Yakunin & Borisova, 1979). Furthermore, in several Al(Ln) alloys the *B2* structure could not be isolated as a single phase material. It is also interesting to point out that the AlCe- and AlDy-type structures consist of fragments of a CsCl array. They show cubes of Al atoms, centered by Ce(Dy) atoms, which are distorted by elongation of one of their edges (see Fig. 4).

Considering that all these alloys, when oxidized, give rise to perovskite-like oxides, it can also be concluded that in these oxides, the insertion of oxygen generates cation structures that correspond to metastable phases of the alloys and that oxidation and pressure could play a similar role in the stabilization of a structure. Thus, the findings reported previously on BaSn (Martínez-Cruz *et al.*, 1994) have been put on a more generalized footing.

In the case of In-containing alloys, the only stable phase is the CsCl type, coinciding with the cation array of the corresponding perovskites.

Another interesting aspect of these perovskites is that the molar volumes of both the oxide and their alloys are similar, as if the insertion of three O atoms per formula would take place without any volume increase. The greatest change (6%) occurs at the couple AlSc–AlScO₃ and might be related to the fact that this phase is only stable under pressure. This feature which has been discussed for four Al(RE)O₃ perovskites (Ramos-Gallardo & Vegas, 1997) can be extended to all the compounds of this series.

Finally some comments should be made on the related Ga-containing compounds Ga(RE)O₃. All the Ga(RE) alloys, except GaEu (not reported) and GaYb (AuCu-type), crystallize in the CrB-type structure. It seems reasonable to assume that they could follow the CrB \rightarrow CsCl transition under pressure and that, hence they will give rise to the

Table 5
Apatite-like compounds.

The cation array of the oxides listed at the top of the table have exactly the same stoichiometry and structure as the corresponding alloy.

Apatite-like compounds	Cation array	Alloy
$Y_5(SiO_4)_3N$	Y_5Si_3	Y_5Si_3 (Mn_5Si_3)
$Ca_5(AsO_4)_3Cl$	Ca_5As_3	Ca_5As_3 (Mn_5Si_3)
$Sr_5(AsO_4)_3Cl$	Sr_5As_3	Sr_5As_3 (Mn_5Si_3)
$Ba_5(AsO_4)_3Cl$	Ba_5As_3	Ba_5As_3 (Mn_5Si_3)
$Ba_5(AsO_4)_2(SO_4)S$	Ba_5As_2S	Ba_5As_3 (Mn_5Si_3)
$CaNd_4(SiO_4)_3O$	$CaNd_4Si_3$	Nd_5Si_3 (Mn_5Si_3)
$CdNd_4(SiO_4)_3O$	$CdNd_4Si_3$	Nd_5Si_3 (Mn_5Si_3)
$La_{4.67}(SiO_4)_3O$	$La_{4.67}Si_3$	La_5Si_3 (Mn_5Si_3)
$CaLa_4(SiO_4)_3O$	$CaLa_4Si_3$	La_5Si_3 (Mn_5Si_3)
$Ce_{4.67}(SiO_4)_3O$	$Ce_{4.67}Si_3$	Ce_5Si_3 (Mn_5Si_3)
$Sm_{4.67}(SiO_4)_3O$	$Sm_{4.67}Si_3$	Sm_5Si_3 (Mn_5Si_3)
$MnSm_4(SiO_4)_3O$	$MnSm_4Si_3$	Sm_5Si_3 (Mn_5Si_3)
$Gd_{4.67}(SiO_4)_3O$	$Gd_{4.67}Si_3$	Gd_5Si_3 (Mn_5Si_3)
$Dy_{4.67}(SiO_4)_3O$	$Dy_{4.67}Si_3$	Dy_5Si_3 (Mn_5Si_3)

corresponding perovskites. In fact, the perovskites $AGaO_3$ ($A = La, Ce, Nd, Gd$) have been reported. For this reason, a high-pressure study of the $Ga(RE)$ alloys is desirable.

$BaGeO_3$ and $BaSiO_3$, listed at the top of Table 4, could well behave like the similar compounds $CaGeO_3$ and $CaSiO_3$, which undergo the transition wollastonite \rightarrow perovskite at 160 kbar (Liu & Ringwood, 1975). If this were true, we would have a nice example of how the $BaGe$ and $BaSi$ subarrays undergo the $CrB \rightarrow CsCl$ transition, even being embedded in the oxygen matrix.

2.8. The apatite structure and the Mn_5Si_3 alloy

Hydroxyapatite $Ca_5(PO_4)_3(OH)$ is a complex structure, which has not been described in depth in structural chemistry. The first satisfactory discussion of the structure is due to Wondratschek *et al.* (1964), who noted that its cation array is isostructural with the Mn_5Si_3 alloy. Even the structure of the alloy is rather difficult to describe. Schubert (1964) considers

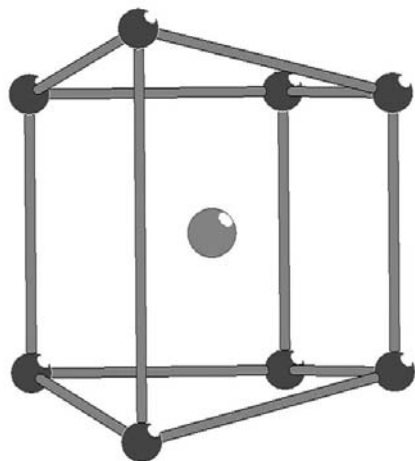


Figure 4
Distorted cube of Al atoms centered by one Ce atom as those existing in the AlCe and AlDy-type structures.

the structure as composed of blocks of both a *h.c.p.* array and β -W. An alternative description is due to Nyman & Andersson (1979) in terms of ‘rosettes’ at $0,0,z$. Finally, Vegas *et al.* (1991) have described the Ca subarray in apatite as formed by blocks of both *h.c.p.* and *b.c.c.* Ca.

An interesting observation of O’Keeffe & Hyde (1985) is that in the isostructural compound $Y_5(SiO_4)_3N$, the Y_5Si_3 subarray is the same as that in the alloy Y_5Si_3 itself. Both structures are represented in Fig. 5. This feature, which was addressed as surprising, must be considered as normal in the light of the results we discuss here and from Table 5. It contains a list of apatite-like compounds in which their cation arrays (Mn_5Si_3 -like) are the same as their corresponding alloys, also of Mn_5Si_3 type. This correspondence is complete in the case of $Y_5(SiO_4)_3N$ and $M_5(AsO_4)_3Cl$ ($M = Ca, Sr, Ba$), but it is somehow modified in the remaining compounds which are all rare-earth silicates. In some of them, stoichiometry requires that the structure be stabilized either by the inclusion of a divalent metal (Ca, Cd or Mn) or by creating defects in the rare-earth positions. However, the existence of $Y_5(SiO_4)_3N$ corroborates this assumption, because when a N atom substitutes a monovalent anion the stoichiometry is fulfilled and the true Y_5Si_3 arrangement is formed.

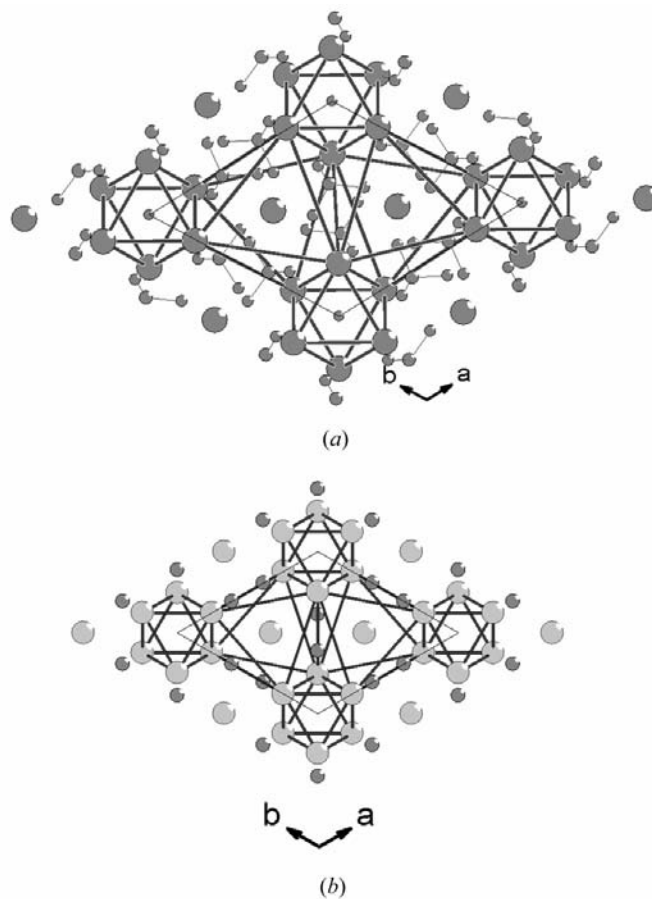


Figure 5
(a) The structure of $Y_5(SiO_4)_3N$ viewed along c , showing the Y atom subarray (connected by contacts) and the SiO_4 units. (b) The structure of Y_5Si_3 viewed in the same projection. To be compared with (a).

Table 6

Comparison of the cation array in some silver oxides with their corresponding alloys.

Alloys	Structure types	Oxides	Cation arrays
AgCl	NaCl, CsCl	AgClO ₂ /AgClO ₃ /AgClO ₄	NaCl/CsCl/NaCl
AgBr	NaCl	AgBrO ₃	CsCl
AgI	Wurtzite, BaAl ₄ , NaCl	AgIO ₃	BaAl ₄
Ag ₂ S	Ag ₂ S	Ag ₂ SO ₃	Ag ₂ S

? >

In the ICSD 20 more apatite-like compounds are referenced, corresponding to the general formulae Cd₅(XO₄)₃Y, where X = P, As, V; Y = Cl, Br, I; M₅(PO₄)₃Cl (M = Sr, Ba); Ca₅(XO₄)₃(OH) (X = P, V, Cr); Ba₅(MnO₄)₃Cl; Sr₅(CrO₄)₃F and several Pb-containing compounds as Pb₅(XO₄)₃Y (X = P, As; Y = F, Cl) and Pb₅(GeO₄)₃(XO₄) (X = S, Cr, V). These compounds cannot be discussed in this context because their corresponding alloys either do not exist under ambient conditions, as is the case for Ca₅P₃, Ba₅P₃ and Cd₅X₃ (X = P, As) or have not yet been investigated. It is possible that the Ca₅P₃ alloy forming the apatite itself could exist under pressure.

It is also interesting to point out that the arystotype Mn₅Si₃ alloy, when oxidized, does not give rise to an apatite-like structure, but to Mn₅(SiO₄)₃ with the garnet structure. It should also be interesting to check whether Mn₅Si₃, under pressure, could transform into a cubic phase with the structure of cations in garnets. Substitution of silicate by phosphate gives rise to the formation of Mn₅(PO₄)₃Cl_{0.9}(OH)_{0.1} with the apatite structure. However, the Mn₅P₃ alloy has not been found under normal conditions and also here, a high-pressure study should be desirable.

2.9. Some silver compounds

The compounds discussed in this section will be the silver halogenates and Ag₂SO₃. They are collected in Table 6 together with their corresponding alloys, the silver(I) halogenides and Ag₂S.

AgCl and AgBr are NaCl-type at ambient conditions and indications have been reported that at high pressures they could transform into CsCl (Bridgman, 1945). In the case of AgCl, the transition sequence NaCl → KOH → TII(CrB) → CsCl has been confirmed recently (Kusaba *et al.*, 1995). AgI, however, forms several polymorphs. At ambient pressure, it adopts the wurtzite structure and at high pressures (~3 kbar) it undergoes two phase transitions. The first leads to a tetragonal net (*P4/n*) in which the Ag and the I atoms are tetra-coordinated by unlike atoms and which is related to the BaAl₄ structure (see Fig. 6), and the second one to a NaCl-type structure. A fourth polymorph (*Im* $\bar{3}$ *m*) exists at high temperatures. It is a superionic compound where the Ag atoms are disordered.

With regards to the oxides, three chlorates have been reported, AgClO₂, AgClO₃ and AgClO₄. AgClO₂ is orthorhombic (*Pcca*) and the cations form a severely distorted NaCl

array. Thus, the insertion of two O atoms only distorts, but does not destroy the structure of the initial alloy AgCl.

Two polymorphs have been reported for AgClO₃. Both are tetragonal (*I4/m* and *I4/mmm*) and their cations form tetragonally distorted arrays of the CsCl type. It seems that the insertion of an additional O atom stabilizes the high-pressure phase of AgCl.

In the case of AgClO₄, two polymorphs have been reported. At room temperature, the structure is tetragonal (*I4* $\bar{2}$ *m*) and the cations form a tetragonally distorted NaCl array. At high temperature (716 K), the structure becomes cubic with a perfect NaCl array and where the anions show rotational disorder. This feature is similar to that observed in the barite group and in the anhydrite group compounds. However, the existence of a NaCl array in AgClO₄ at room temperature is an unexpected result. Following the behaviour of the other oxides, it seems reasonable that by increasing the oxygen contents to 4, the cations would have adopted a high-pressure structure of the alloy. In spite of this singular exception it can be stated again that the oxides stabilize the structures of the corresponding alloys.

AgBrO₃ is the only reported oxide which is derived from AgBr. It is isostructural with one of the tetragonal phases (*I4/mmm*) of AgClO₃ and hence, cations are arranged as in CsCl which is a plausible high-pressure phase of AgBr.

The cation array of AgIO₃ is represented in Fig. 7. Although the structure seems rather complicated, a rational description can be made when referring to the high-pressure phase of AgI, which is represented in Fig. 6. AgI, as mentioned previously, is related to BaAl₄. It consists of 4⁴ nets of Ag atoms, whose squares are capped, alternatively up and down, by I atoms. The result is that each 4⁴ silver net is situated midway between two 4⁴ layers of I atoms. These three layers form blocks perpendicular to *c* and are stacked in an ...AAA... sequence in such a way that each I atom of the upper block caps the I₄ squares of the lower block. This arrangement results in each Ag atom being tetrahedrally coordinated by four I atoms and each I atom bonding to four Ag atoms forming the squares and giving rise to square pyramids. The 'bonding' scheme in AgIO₃ is the same. The difference is that the silver 4⁴ nets are no longer planar, but they are puckered (acordion-like conformed). This produces a change in the geometry of the coordination spheres around the Ag atoms, which is no longer tetrahedral. The other structural features remain as in AgI. It can be concluded that the insertion of O atoms in an AgI framework only produces a deformation of the structure.

**Figure 6**

Stereopair showing the tetragonal structure of AgI. Grey and black circles represent Ag and I atoms, respectively. The structure is related to the Al subarray in BaAl₄.

Again, oxidation gives rise to the stabilization of a high-pressure phase of the alloy.

The last compound we will comment in this section is Ag_2SO_3 , together with its parent alloy Ag_2S . The structures of both compounds are represented in Figs. 8 and 9 and as can be seen the topology of the Ag_2S array is the same in both the alloy and the oxide. A new example of how the structure of a given alloy is maintained in the oxide is shown. We have also examined the Ag_2S topology in Ag_2SO_4 , but the structures are not related, probably as a consequence of the increase in the oxygen contents. Unfortunately, there is no data available on possible phase transitions in Ag_2S under pressure to be compared with the cation array in the sulfate.

2.10. The $\text{CaF}_2 \rightarrow$ cotunnite $\rightarrow \text{Ni}_2\text{In}$ transitions and related oxides

The structures of CaF_2 , PbCl_2 (cotunnite) and Ni_2In are closely related. Several compounds such as MF_2 ($M = \text{Ca}, \text{Sr}, \text{Ba}, \text{Cd}, \text{Pb}, \text{Eu}$), SrCl_2 and MO_2 ($M = \text{Ce}, \text{Pu}, \text{Th}$) undergo, under pressure, the fluorite \rightarrow cotunnite phase transition (Dandekar & Jamieson, 1969; Gerward *et al.*, 1992; Beck, 1979; Duclos *et al.*, 1988; Dancausse *et al.*, 1990). The same transition has recently been observed in Li_2S (Grzechnik *et al.*, 2000). At higher pressures, some compounds, such as BaF_2 (Leger *et al.*, 1995) and Na_2S (Vegas *et al.*, 2001), undergo a second phase transition from cotunnite to Ni_2In . On the other hand, the same transition $\text{PbCl}_2 \rightarrow \text{Ni}_2\text{In}$ has been observed at high temperatures in Ni_2Si (Toman, 1952). This feature is difficult to understand because the CN of cations (Ba^{2+} in BaF_2) increases, from 8 in fluorite to 9 in cotunnite and to 11 in Ni_2In , by increasing the pressure, but in Ni_2Si the higher CN occurs at high temperature which is just the opposite to high pressure. This indicates that the aforementioned structural transformations must conform not only to the effect of pressure, but to other additional factors not yet understood. Nevertheless, these three structures seem to be intimately related. The structures of cotunnite and Ni_2In are represented in Figs. 10 and 11.

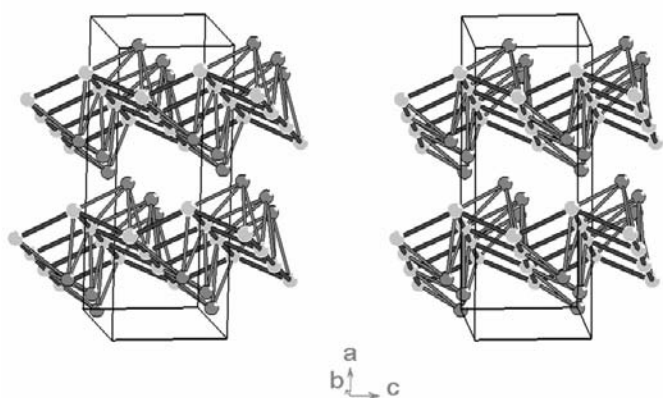


Figure 7
The cation array of AgIO_3 . It is formed by corrugated sheets of Ag atoms (white circles) capped by I atoms. To be compared with Fig. 6.

The structures of cotunnite and of Ni_2In also appear in the cation subarray of many oxides. O’Keeffe & Hyde (1985) reported for the first time on the cation array of $\beta\text{-K}_2\text{SO}_4$ and $\beta\text{-Ca}_2\text{SiO}_4$ and of many other isostructural compounds (about 35) listed by Wyckoff (1965) to correspond to the cotunnite structure. They also realised that the cotunnite structure, present in $\beta\text{-Ca}_2\text{SiO}_4$, is the structure of the Ca_2Si alloy itself. This was considered as a ‘striking structural relationship’. Moreover, the insertion of four O atoms per formula unit occurs with a volume increase of only 3.8%. However, from the compounds listed in Table 7 it can be concluded that this

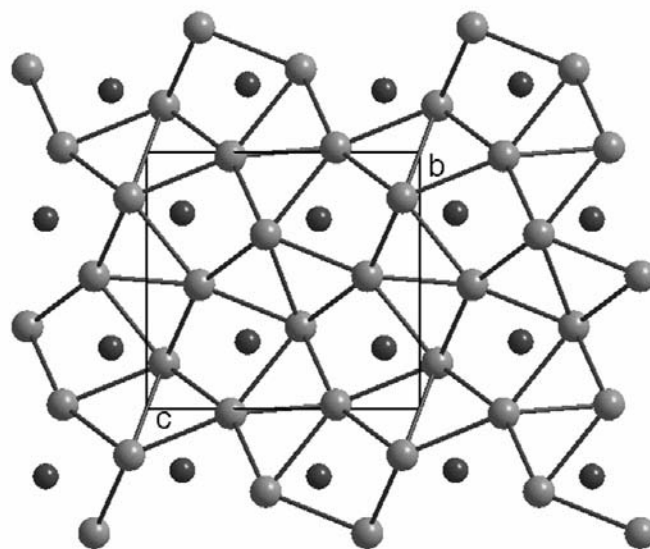


Figure 8
The structure of Ag_2S . Grey and black circles represent Ag and S atoms, respectively. The Ag–Ag contacts are represented.

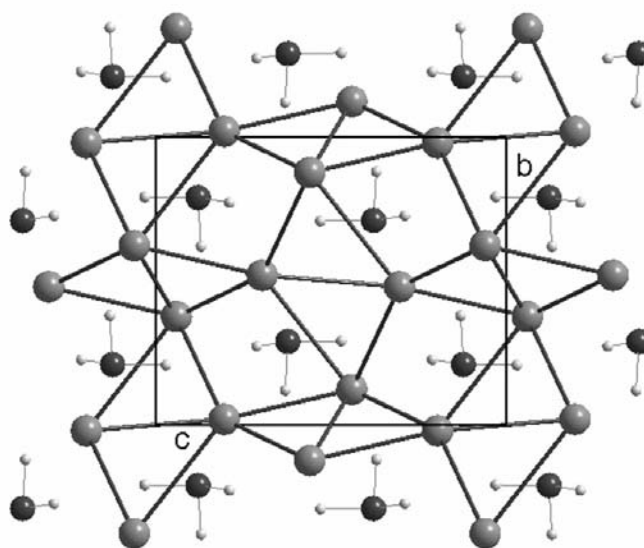


Figure 9
The structure of Ag_2SO_3 showing the Ag skeleton represented by grey atoms bonded by contacts and the SO_3 units (black circles). As seen when compared with Fig. 8, the two structures have the same Ag_2S structure. The origins of both unit cells are displaced with respect to each other.

Table 7

Compounds whose cation arrays are of the cotunnite (PbCl₂)-type or Ni₂In-type.

They have the same structure as their corresponding alloys.

Alloys	Structure types	Oxides	Cation arrays
Li ₂ S	CaF ₂ , Li ₂ S, PbCl ₂	Li ₂ SO ₄	CaF ₂ , Li ₂ S
Ca ₂ Si	PbCl ₂	Ca ₂ SiO ₄	PbCl ₂
Sr ₂ Si	PbCl ₂	Sr ₂ SiO ₄	PbCl ₂
Ba ₂ Si	PbCl ₂	Ba ₂ SiO ₄	PbCl ₂
Sr ₂ Ge	PbCl ₂	Sr ₂ GeO ₄	PbCl ₂
Cs ₂ S	PbCl ₂	Cs ₂ SO ₄	PbCl ₂
Cs ₂ Se	PbCl ₂	Cs ₂ SeO ₄	PbCl ₂
Na ₂ S	CaF ₂ , PbCl ₂ , Ni ₂ In	NaKSO ₄	PbCl ₂
Na ₂ S	CaF ₂ , PbCl ₂ , Ni ₂ In	Na ₂ SO ₄	Ni ₂ In
K ₂ S	CaF ₂ , Ni ₂ In	K ₂ SO ₃ /K ₂ SO ₄	Ni ₂ In/Ni ₂ In
Ni ₂ Si	PbCl ₂ , Ni ₂ In	Ni ₂ SiO ₄	Ni ₂ In
CoMnSi	Ni ₂ In	CoMnSiO ₄	Ni ₂ In
KZnP	Ni ₂ In	KZnPO ₄	Ni ₂ In
Mn ₂ Ge	Ni ₂ In	Mn ₂ GeO ₄	Ni ₂ In

relationship is not unique and that at least seven compounds behave in the same manner, stabilizing in the oxide the structure of the alloy itself. In the case of Na₂S, there is no oxide whose cation array has the cotunnite structure, but partial substitution by K stabilizes this arrangement which is a high-pressure phase of Na₂S (Vegas *et al.*, 2001).

Also in Table 7 are listed the oxides whose cation array is of the Ni₂In type. Ni₂SiO₄ also has an anomalous behaviour, stabilizing the high-temperature form of the alloy Ni₂Si. It is isomorphous with olivine as it is Mn₂GeO₄. KZnPO₄, K₂SO₃ and HT-K₂SO₄ are isostructural with olivine, but they have a hexagonal symmetry as in the Ni₂In-type structure. Na₂SO₄ has three high-temperature phases, two orthorhombic, one of which is isostructural with olivine and one hexagonal which reproduces exactly the topology and symmetry of the HP-Na₂S. All these compounds are ‘real stuffed alloys’ of the Ni₂In-type.

The sulfides Li₂S, Na₂S and K₂S and their corresponding sulfates merit a deeper consideration.

As mentioned previously, Na₂S undergoes the antifluorite → anticotunnite → Ni₂In phase transitions (Vegas *et al.*, 2001). It is also well known that olivine, Mg₂SiO₄, transforms at very high pressures into spinel. Since olivine has a cation array of the Ni₂In type and spinel that of the MgCu₂ type (O’Keeffe & Hyde, 1985), the transition path could follow the sequence fluorite → cotunnite → Ni₂In → MgCu₂. The last step has never been observed. However, when we notionally insert oxygen into Na₂S and form the mineral thenardite, which is the room-temperature form of Na₂SO₄, cations arrange in such a manner that fragments of a spinel structure can be recognized. The impression is that insertion of four O atoms produces an internal pressure almost high enough to attain the MgCu₂ array. The question which arises is if under pressure thenardite could be converted in the first sulfate spinel. When thenardite is heated, that is, the pressure is released, it converts into an olivine-like structure with the Ni₂In array, a further example of how high-temperature stabilizes the lower pressure phase of the alloy.

In the case of K₂S, preliminary results (Vegas *et al.*, 2002) indicate that up to 10.8 GPa there are two phase transitions. The first one occurs at very low pressures and its structure could not yet be solved. The second one occurs at 6.0 GPa, where the Ni₂In-type structure appears. It is quite possible that at higher pressures the anticotunnite phase could be stabilized and that K₂S could follow an anomalous transition path as it does Ni₂Si. Thus, if the anticotunnite structure would be the higher-pressure phase, then the Ni₂In phase would be equivalent to a high-temperature (lower pressure) phase. The reported data on K₂SO₃ and K₂SO₄ are consistent with this. K₂SO₃ has a cation array of the Ni₂In type. It seems that the insertion of three O atoms produces a pressure which is sufficient to stabilize the low-pressure phase. However, when four O atoms are inserted, then the high-pressure phase (anticotunnite) is formed, as occurs in β-K₂SO₄. However, when this phase is heated, the lower-pressure phase (Ni₂In) is recovered as in HT-K₂SO₄.

With regards to Li₂S, its high-pressure behaviour has been investigated up to 20.8 GPa (Grzechnik *et al.*, 2000). By compression, the antifluorite → anticotunnite reversible phase transition occurs at 12 GPa. However, in the decompression region (at 7.9 GPa) the anticotunnite structure passes through an intermediate structure which shows some unusual features. It consists of an *h.c.p.* array of S atoms with all tetrahedral holes occupied by Li atoms. In this structure (Grzechnik *et al.*, 2000), the Li atoms form a distorted four-connected net which is related to the wurtzite skeleton. An

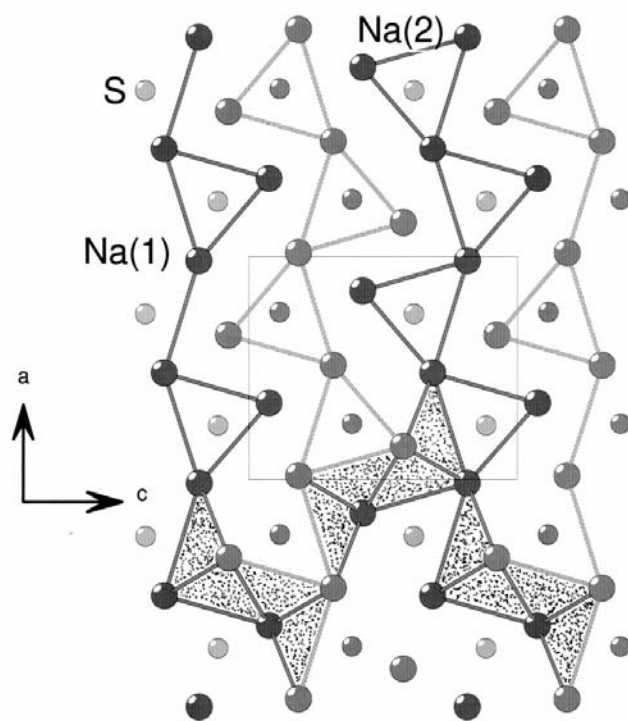


Figure 10
The anticotunnite structure formed by Na and S atoms in Na₂S at high pressures. Large circles: Na atoms; small circles: S atoms; black and grey circles are displaced *b*/2 with respect to each other.

Table 8

Miscellaneous compounds whose cation arrays are the same than those of the corresponding alloy.

Alloys	Oxides	Structure of the cation array
K ₂ S ₂	K ₂ S ₂ O ₆	NiAs
Rb ₂ S ₂	Rb ₂ S ₂ O ₆	NiAs
CuCl ₂	Cu(ClO ₄) ₂	Chains with bridging chlorides
NiP	Ni ₂ P ₂ O ₇	Graphites of Ni with P ₂ dimers
CoP ₂	Co ₂ P ₄ O ₁₂	Squares of P atoms
In ₂ S ₃	In ₂ (SO ₄) ₃	Corundum
TiB	TiBO ₃	NaCl (calcite)
EuS	EuSO ₄	NaCl
Rb ₃ Bi	Rb ₃ BiO ₃	BiF ₃ (Fe ₃ Al)
Cs ₃ Bi	Cs ₃ BiO ₃	BiF ₃ (Fe ₃ Al)
Ca (<i>f.c.c.</i>)	CaF ₂	<i>f.c.c.</i>
Ca (<i>s.c.</i>)	CaO (CsCl)	<i>s.c.</i>

inspection to the cation arrays of Li₂SO₄ (room temperature) and Li₂SeO₄ revealed that the former is a distortion of the phenakite (Be₂SiO₄) structure, whereas the latter is isostructural with it. The structure of phenakite is represented in Fig. 12 and as can be seen it is also formed by a four-connected net of Be atoms, which is strongly related to that of Li₂S. Thus, the structure of the metastable HP phase of Li₂S is almost reproduced in Li₂SO₄ and in Li₂SeO₄. It is really surprising that such an unusual structure can be found in both the alloy and the oxide. When Li₂SO₄ is heated, the compound transforms to a cubic phase with the Li and S atoms arranged as in antifluorite. Again, temperature, opposite to pressure, allows the ambient pressure phase to be recovered.

2.11. Rare earth phosphates (monazites)

This structure type was briefly discussed when we considered SrSeO₄ and PbSeO₄. It is adopted by the earlier rare

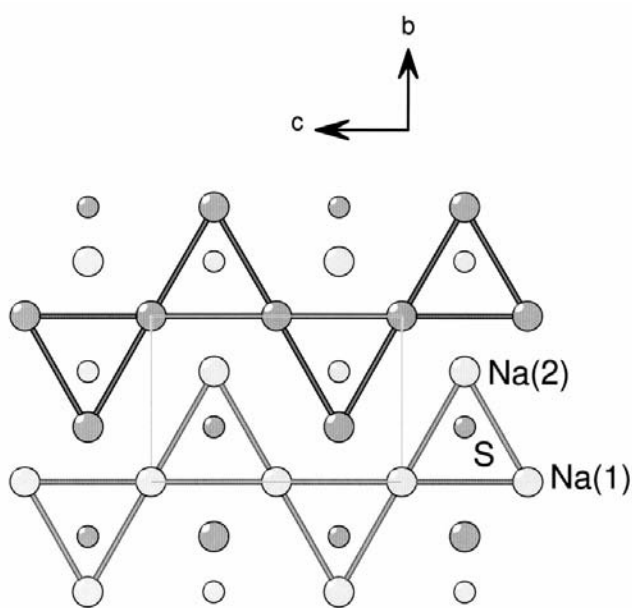


Figure 11
The Ni₂In-type structure adopted by Na₂S under pressure. Contiguous chains of trigonal prisms are displaced by *a*/2.

earth phosphates (RE)PO₄ (RE = La, Ce, Pr, Nd, Sm, Eu and Gd). The remaining rare earth phosphates crystallize in the xenotime (YPO₄) structure. On the other hand, all the binary phosphides (RE)P adopt the NaCl structure.

The monazite structure is represented in Fig. 13. It can be described as a heavily distorted NaCl structure in which all the {002} planes are puckered. The result is that the small cubes (one eighth of the NaCl unit cell), which have their corners occupied alternatively by (RE) and P atoms, become triclinic prisms in monazite. Half of these prisms are so distorted to such an extent that an additional contact is produced between one Ce and one P atom. These atoms occupy opposite corners in the prisms. If these additional contacts would occur in all the prisms, each atom (Ce, P) would be surrounded by eight unlike atoms, but because they occur only in alternate prisms the CN is 7. Thus, the CeP subarray can be seen as a distorted NaCl structure in which the CN increased from 6 to 7. Obviously, oxidation has produced the same effect as pressure again. As we have discussed in other sections of this paper, it could well be possible that at high temperature (equivalent to decompression) a more regular framework of the CeP subarray could be obtained or even the NaCl structure of CeP could be recovered.

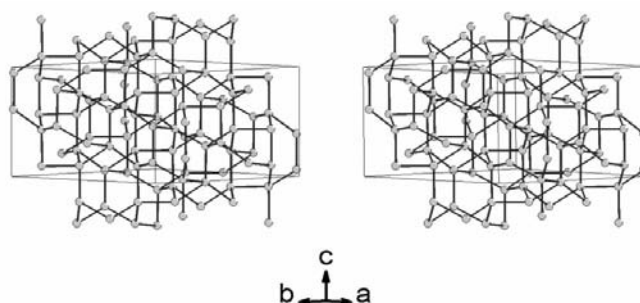


Figure 12
Stereopair showing the Be subarray in phenakite Be₂SiO₄. They form a four-connected net in which fragments of a wurtzite-like structure are present. Remember that a wurtzite-like structure is that adopted by the Li atoms in the high-pressure phase of Li₂S.

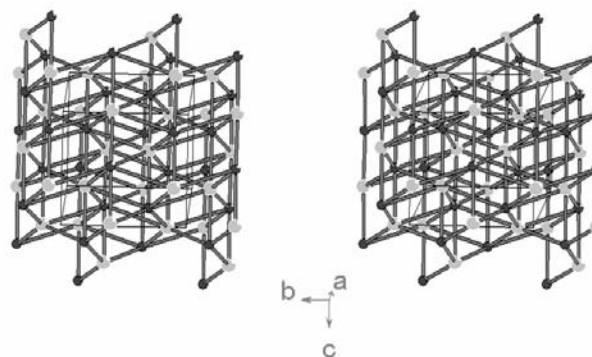


Figure 13
Stereopair showing the cation array in monazite (CePO₄). As shown a very distorted NaCl-type structure is formed, in which each atom type is coordinated by seven unlike atoms.

2.12. Miscellaneous compounds

The compounds discussed in this section are collected in Table 8. They belong to very different structural families but have in common the maintenance of the structure of the alloy in their oxides. Some of them show simple structures, but other ones exhibit very uncommon frameworks.

K_2S_2 and Rb_2S_2 adopt the NiAs structure in which an *h.c.p.* of alkali atoms shows all the octahedral sites as occupied by S atoms. Owing to the existence of S–S bonds, the S atoms are slightly off-center of the octahedra. When O atoms are inserted to produce the disulfate $M_2S_2O_6$ ($M = K, Rb$), the alkali atoms and the S atoms remain in the same mutual arrangement.

TiB and EuS adopt the NaCl-type. When they form the oxides $TiBO_3$ and $EuSO_4$, the NaCl array is kept. In the case of titanium orthoborate (calcite-like) the cation array is a rhombohedral distortion of the NaCl structure ($\alpha = 76.33^\circ$).

In Rb_3BiO_3 and Cs_3BiO_3 (Zoche & Jansen, 1997*a,b*) the structure of the alloys Rb_3Bi and Cs_3Bi , which are of the BiF_3 (Fe_3Al) type, are retained. Also in this case, the insertion of oxygen takes place without any volume increase. Even a slight contraction of the molar volume is observed for the oxides as compared to the binary alloys.

Three phases of In_2S_3 are known. Two of them are ambient pressure phases. The first is a defective spinel and the second has been related to the Laves phases. The third is a high-pressure phase (Range & Zabel, 1978; synthesized at 3.5 GPa and 773 K) and has the corundum structure. The corre-

sponding oxide $In_2(SO_4)_3$ has two modifications. The first, stable at room temperature, presents a complicated structure where the In atoms form a three-dimensional net of five-connected indium. At high temperature the sulfate transforms to a rhombohedral structure ($R\bar{3}$), in which the In_2S_3 subarray has the corundum structure. Thus, the high-temperature phase of the oxide has adopted the HP structure of the alloy.

Two calcium binary compounds CaF_2 and CaO also show an interesting behaviour. Fluorite consists of an *f.c.c.* array of Ca atoms with F atoms occupying all the tetrahedral interstices. As pointed out by O'Keeffe & Hyde (1985), the unit-cell dimensions of both *f.c.c.*-Ca and CaF_2 are almost the same (a contraction of 6.6% in the molar volume is observed in fluorite). On the other hand, CaO is an NaCl type, but at high

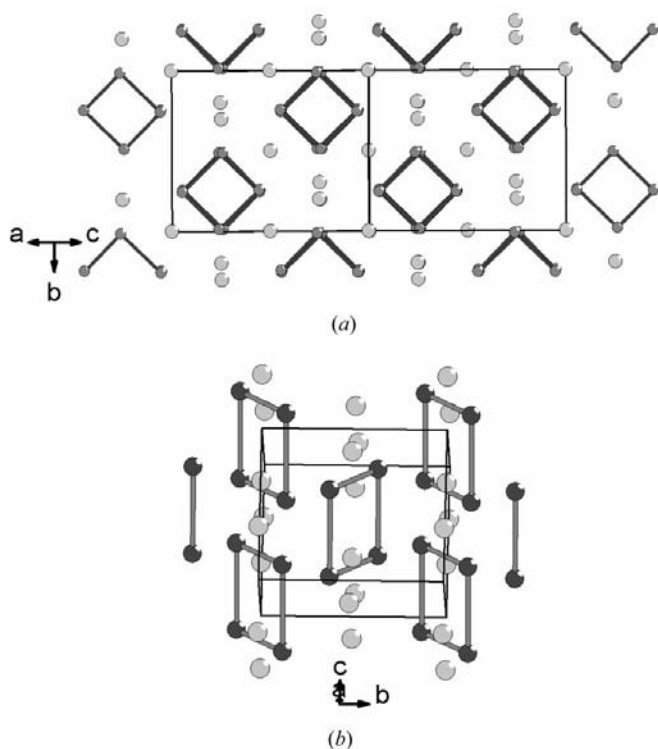


Figure 14

(a) The cation array in $Co_2P_4O_{12}$, showing the Co atoms (white circles) and the P_4 squares. P–P contacts have been drawn. (b) The P_4 rectangles are observed in CoP_2 .

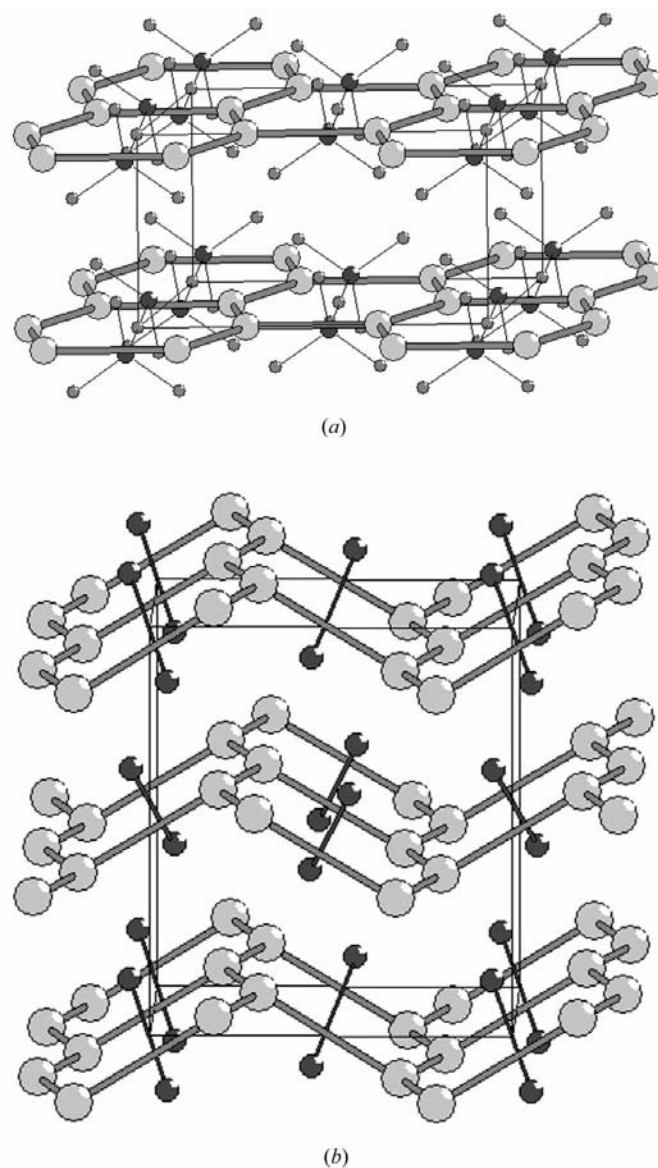


Figure 15

(a) The graphite-like structure formed by the Ni atoms in $Ni_2P_2O_7$. The P_2O_7 units (black circles) are inserted into the Ni_6 hexagons. (b) The corrugated graphite-like network of Ni atoms in NiP . The P_2 dumbbells are also inserted into the Ni_6 hexagons.

pressures it transforms into a CsCl-type structure. Its unit-cell dimension is 2.64 Å. This value is, within 1%, in agreement with 2.615 Å, as found in the simple cubic structure of elemental Ca at 39 GPa (Olynyk & Holzapfel, 1984).

The CuCl₂ subarray in Cu(ClO₄)₂ is formed by infinite planar chains of Cu atoms bonded to four bridging Cl atoms. This is just the structure adopted by the dihalide CuCl₂ itself.

In Co₂P₄O₁₂, the structure is composed of Co²⁺ cations and cyclotetraphosphate anions. It almost corresponds to the conformation adopted by P atoms in the CoP₂ phosphide, where P atoms form rectangles (see Fig. 14).

Also in Ni₂P₂O₇, the similarity is surprising. The Ni atoms form parallel graphite-like layers with P₂ dumbbells situated at the centre of the rings and perpendicular to them (see Fig. 15). Just the same structure can be found in the NiP phosphide!

3. Discussion

The results presented here contain more than 100 examples of oxides whose cation arrays are topologically related to the structure of their corresponding alloy. The coincidences found by O'Keeffe & Hyde (1985), Martínez-Cruz *et al.* (1994), Ramos-Gallardo & Vegas (1997) and Zoche & Jansen (1997*a,b*) can no longer be seen as striking relationships. It seems more reasonable to see them as examples of a general trend in the structures of oxides.

Among the examples given, one must distinguish between those compounds for which the similarity is merely topological, as in RbCl and RbClO₃, showing the expanded structure of the corresponding alloy, and those compounds in which both alloy and oxide have the same topology and cell dimensions (molar volumes) as if the O atoms simply occupied the vacant sites of the corresponding alloy (element) structure. Within this group we can include BaGeO₃, CaF₂, CaO (CsCl), Ca₂SiO₄, BaSnO₃, (RE)AlO₃, Rb₃BiO₃ and Cs₃BiO₃. The reasons for the different behaviour are not yet understood.

What is true, however, is that cations do not arrange in a more or less arbitrary way, but try to reproduce the structure of their corresponding alloy. Cations do not seem to be the 'isolated entities' which occupy interstices of an oxygen matrix. They could be more important than believed in determining the structure of oxides. This principle has clearly been formulated by Liebau (1999) when he said: the stability of the structure is primarily determined by the high symmetrical potential distribution of the cations.

A first aspect that deserves a closer inspection is why in some cases, apatite for instance, cations reproduce the structure of the ambient pressure phase of the alloy, whereas in other cases cations arrange as the high-pressure phases. A possible explanation could be that the arrangement in the oxide depends on the pressure range stability of a given alloy phase. If the pressure needed to produce a phase transition is very high, then the ambient pressure phase remains in the oxide. On the contrary, if phase transitions occur at relatively low pressures, then the high-pressure structure can be stabilized in the oxide. The data on alkali chlorates are in agreement with this view. The B1 → B2 transitions in the alkali

chlorides take place at 300 kbar in NaCl, at 20 kbar in KCl and at 5 kbar in RbCl. Consequently, NaClO₂, NaClO₃ and NaClO₄ all show a distorted B1 structure and the B2 structure is never attained. KClO₃ adopts the stuffed CrB-type structure, but an additional pressure of only 6 kbar transforms this structure into a distorted B2 array. Finally, RbClO₃ adopts the B2 structure at ambient pressure. The behaviour of Na₂SO₄ discussed above is also in agreement with this explanation.

Another interesting aspect is that, in many examples, the oxide is reproducing the topology of the high-pressure phases of the alloy, suggesting an equivalence between oxidation and pressure as was firstly proposed in the case of BaSnO₃ (Martínez-Cruz *et al.*, 1994). The examples given here for alkali halogenates, MnSeO₄, ZnSO₄, ZnSeO₃, LaAlO₃, CeAlO₃, PrAlO₃, SmAlO₃, silver halogenates, Li₂SO₄, Na₂SO₄, K₂SO₄ and In₂(SO₄)₃ are lending support of this idea. At present, explanations can only be given at a qualitative level, but a quantification of the pressure exercised by O atoms on the cation array should be desirable. We believe that this is an interesting open question. To quantify this effect several factors must be taken into account and not only the oxygen contents. Thus, in RbClO₃ three O atoms stabilize a CsCl structure (CN = 8), but in RbClO₄ cations adopt the FeB structure where each atom is coordinated by only seven unlike atoms. A possible explanation of this CN decreasing at 'high pressures' could be that in the FeB structure, two additional like atoms are situated at shorter distances than the seventh unlike atom, so that the CN would be really 9 (7 + 2). Similar arguments can be used to explain the differences between CsIO₃ and CsIO₄. The former has a CsCl structure, the latter a scheelite-like structure where each atom is surrounded by eight unlike atoms and, at the same distances, by four like atoms (CN = 12). In spite of these possible anomalies, the general trend seems to be that, in the oxides, the CN between cations increases and that, when heated, this CN decreases, recovering in many instances the ambient pressure structure of the alloy. The examples of alkali halides and ZnS are illustrative. Surely, new experiments on the behaviour of oxides at high temperature and of alloys at high pressures will give new data which will help us to better understand the role of oxygen.

In the light of the structures discussed here, it seems clear that the descriptive model of O'Keeffe & Hyde (1985) is also physically meaningful. The structures of oxides are 'unaltered stuffed alloys' where the structure of the alloy remains. In our opinion, this 'new proposal' represents an advance with respect to the merely descriptive model. When KClO₃ is described as a KCl array of the CrB-type stuffed with O atoms, it does not mean that the CrB array is a curious coincidence. It means that this array is more than plausible in KCl. The recent discovery of this array in NaBr and NaI (Leger *et al.*, 1998) is underlying that this is not a strange framework for the alkali halides, including KCl. When they are describing olivine as a Mg₂Si array of the Ni₂In-type, it means that this array could be more than probable in view of the fluorite-like structure of Mg₂Si and of the transitions sequence fluorite → cotunnite → Ni₂In.

In the same manner, the fact that the MIO_4 ($M = Na, K, Rb, Cs$) crystallize in the scheelite-type structure could be seen as a hazardous feature. However, when we know that CsI deposited in thin layers crystallizes in a closely related structure, the relationship is physically sound. We believe that the structures of oxides are better understood when we look at the cation arrays. Many of the phase transitions and the polymorphism of oxides described here are better explained when they are considered as formed by previous entities which are the alloys.

We do not believe that all these features are casual. It seems that cations recognize themselves in spite of being embedded in an oxygen bulk. The nature of this recognition and its physical meaning are at present a great problem which remains unsolved. We hope that further work will be made in order to elucidate this question.

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