

The Cu_2Sb and related structures

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Abstract. It is observed that neither inspection of z values, consideration of near-neighbour coordination, nor chemical considerations show in all cases which atom occupies site $2(c_1)$ and which site $2(c_{II})$ of the Cu_2Sb $tP6$ structure. Calculation of the *Wirkungsbereiche* by the Dirichlet construction shows indisputably which site is which. Assignments are made for all phases whose z values have been determined. Separation of phases with the Cu_2Sb structure into two groups is effected on chemical considerations and observed physical properties.

Wirkungsbereiche, near-neighbour coordination, and framework descriptions of the structure are discussed, as well as related derived structure types. Stability and availability of the structure is discussed in relation to the number of valency electrons provided by the component atoms.

1. Introduction

The Cu_2Sb $tP6$ structure is described in $P4/nmm$ with atoms in $2(a)$ $0, 0, 0$; $2(c_1)$ $0, 1/2, z_1$ and $2(c_{II})$ $0, 1/2, z_{II}$; origin at $\bar{4}m2$. A perpetual muddle, embraces interpretation of published structural data on phases with the structure, since z_1 and z_{II} values are so similar that it is impossible to tell by inspection which is site $2(c_1)$ and which is $2(c_{II})$. In addition descriptions $2(c_1): 0, 1/2, z_1, 2(c_{II}): 0, 1/2, z_{II}$ and $2(c_1): 0, 1/2, \bar{z}_1, 2(c_{II}): 0, 1/2, \bar{z}_{II}$ result in identical interatomic distances and coordination polyhedra, so it is not significant that z_1 or z_{II} has the larger value. Furthermore although z_{II} is generally larger than z_1 , this is not always so. Even near-neighbour coordination numbers do not always permit determination of $2(c_1)$ and $2(c_{II})$. For example Mn_2Sb has Sb on $2(c_{II})$ whereas Mn_2As has As on $2(c_1)$, nevertheless both Sb and As have nine close neighbours, whereas Mn(2) has five close neighbours on $2(c_1)$ in Mn_2Sb and on $2(c_{II})$ in Mn_2As . Chemical evidence is no aid to determining which position is $2(c_1)$ and which is $2(c_{II})$. Formulae of known phases with the structure can be represented as M_2X , $\text{M}'\text{M}''\text{X}$, MX_2 and $\text{MX}'\text{X}''$, where M are

metal atoms and X are elements from Groups IV to VI excluding transition metals of these Groups. The $2(c_{II})$ position, for example, can be occupied either by M or X atoms.

In order to determine which site is $2(c_I)$ and which is $2(c_{II})$, it is necessary to determine the coordination polyhedra, by the Dirichlet (1850) construction, since the *Wirkungsbereiche* so obtained follow two quite distinct series of shapes as the axial ratio of the phases changes between the limiting values of approximately 1.45 and 2.6. This procedure leaves no doubt which of the two $2(c)$ sites is which. We have carried out sufficient calculations of the *Wirkungsbereiche* of phases with the structure to assign atoms to $2(c_I)$ and to $2(c_{II})$ for all phases the atom positions of which have been determined, and report our results here.

Such calculations introduce a puzzling feature for those conditioned to finding in the structures of intermetallic phases that the largest atoms occupy coordination polyhedra with the largest number of corners (neighbours) – as determined by the Dirichlet construction. In these phases the smallest atom *may* occupy the coordination polyhedron that has the largest number of corners – but of course the polyhedron (or *Wirkungsbereich*) despite its greater number of corners (or faces) has a smaller volume than that (those) occupied by larger atoms(s).

Nearly 200 phases are known to have the Cu_2Sb structure. Their axial ratios, c/a , vary from about 1.45 to 2.6, and the difference $\bar{z}_{II} - z_I$ varies from about -0.01 to 0.20 . The smallest differences are found in phases with small axial ratios. Phases contain atoms whose coordination number (CN) 12 diameters range between about 1.8 \AA and 4.75 \AA , and the ratio of the diameter of the largest to the smallest atom found in individual phases ranges from about 1.0 to 2.0.

In this paper when discussing atomic size we use the CN 12 diameters of Teatum et al. (1960). *Wirkungsbereiche* have been calculated by the method of Fischer et al., 1971 (*Potenzebenen* construction). Structural details of phases discussed can be found in Pearson (1967) or result from the recent literature search of Villars (1984).

2. Structural chemistry and geometry

Table 1 lists phases with the Cu_2Sb structure for which atomic positions have been determined, and shows our assignment of atoms to $2(c_I)$ and $2(c_{II})$ sites. It shows the coordination numbers of the three sites determined by the Dirichlet construction and also by comparison of interatomic distances and radius sums, where only those atoms separated by distances less than, or not much greater (say $< 0.10 \text{ \AA}$) than the radius sums are considered to be neighbours. Several of these arrangements are indicated in Figs. 1 and 2. Comparison of the coordination numbers obtained by Dirichlet construction for atoms on $2(c_I)$ and $2(c_{II})$ shows that they can be uniquely assigned by this

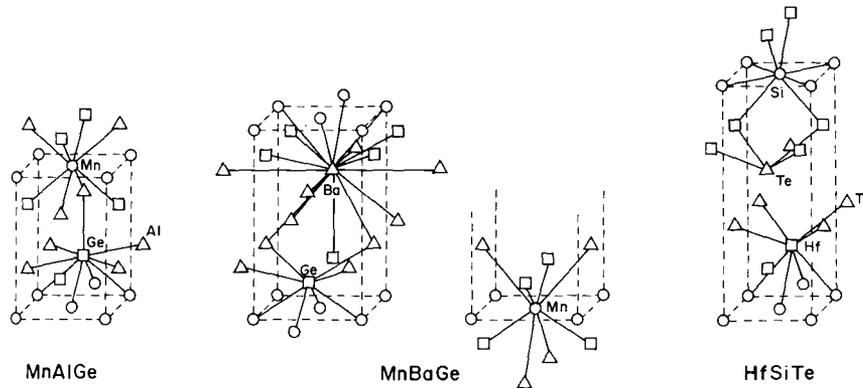


Fig. 1. Close neighbours about the atoms in MnAlGe ($c/a=1.516$), MnBaGe ($c/a=1.760$) and HfSiTe ($c/a=2.651$) with the Cu₂Sb structure

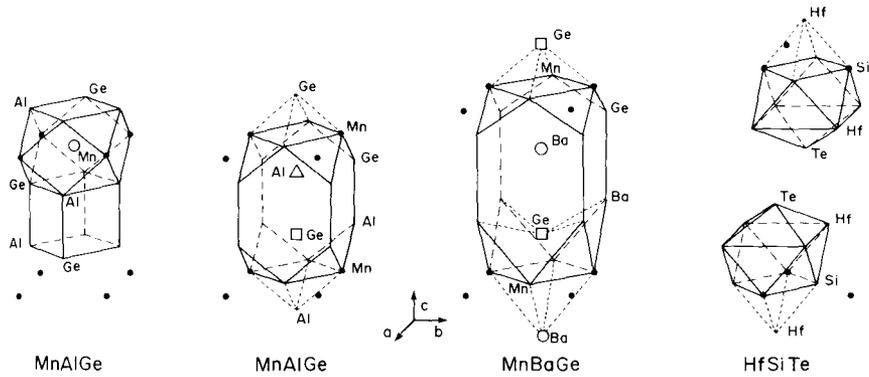


Fig. 2. Various close-neighbour coordination polyhedra surrounding the atoms in MnAlGe, MnBaGe and HfSiTe with the Cu₂Sb structure. Black dots indicate the corners of the unit cell

means. This is further apparent from the series of *Wirkungsbereiche* for the two sites shown in Fig. 3 below.

A separation of phases with the Cu₂Sb structure can be effected according to the chemical nature of the component atoms and the physical properties of the structure.

Phases M₂X and M'M''X occur generally in the range of axial ratios from $c/a=1.45$ to 1.80, although VZrSi and VHfSi have axial ratios of 1.95. z_{II} values range from about 0.62 to 0.67 and z_I values from about 0.19 to 0.26 except for the binary phases and MnAlGe, FeLiAs, FeLiP and MnZnSb where z_{II} values extend to 0.76 and z_I to 0.303. In these phases it appears that the larger atom always occupies site 2(c_{II}), although CuMgAs, Fe₂As, Mn₂As and Cr₂As appear to be exceptions to this rule that will be discussed below. Thus in phases with axial ratios up to $c/a=1.610$ it is the X atom that occupies

Table 1. Phases with the Cu₂Sb structure, with atomic parameters determined
M₂X and M'M'X phases

Phase	<i>a</i> (Å)	<i>c</i> (Å)	<i>c/a</i>	2(<i>a</i>) atom		2(<i>c</i> _I)		2(<i>c</i> _{II})			Wirkungsbereiche, no. of faces			Coordination polyhedron no. of close neighbours		
				atom	<i>z</i> _I	atom	<i>z</i> _{II}	site 2(<i>a</i>)	2(<i>c</i> _I)	2(<i>c</i> _{II})	site 2(<i>a</i>)	2(<i>c</i> _I)	2(<i>c</i> _{II})			
MnZnSb*	4.173	6.233	1.494	Mn	Zn	0.2808	Sb	0.7160	12	10	18	4 Zn, 4 Sb	1 + 4 Sb, 4 Mn	1 + 4 Zn, 4 Mn		
MnAlGe*	3.914	5.933	1.516	Mn	Ge	0.280	Al	0.727	12	10	18	4 Al, 4 Ge	4 Mn, 1 + 4 Al	4 Mn, 1 + 4 Ge		
Cu ₂ Sb*	4.0006	6.1043	1.526	Cu(1)	Cu(2)	0.270	Sb	0.70	12	10	18	4 Cu(2), 4 Sb	4 Cu(1), 1 + 4 Sb	1 + 4 Cu(2), 4 Cu(1)		
Cu ₂ As*	3.788	5.942	1.569	Cu(1)	Cu(2)	0.303	As	0.709	12	10	18	4 As, 4 Cu(2)	1 + 4 As, 4 Cu(1)	1 + 4 Cu(2), 4 Cu(1)		
CuMgAs*	3.961	6.238	1.575	Cu	Mg	0.250	As	0.665	12	14	18	4 Mg	4 Cu, 1 + 4 As	1 + 4 Mg		
(Ni _{3.14} Te ₂)	3.782	6.062	1.603	Ni(1)	Ni(2)	0.31	Te	0.71								
Mn ₂ Sb*	4.078	6.557	1.608	Mn(1)	Mn(2)	0.2897	Sb	0.7207	12	10	18	4 Sb	1 + 4 Sb	4 Mn(1), 1 + 4 Mn(2)		
MgNaAs*	4.422	7.138	1.614	Mg	As	0.2234	Na	0.6539								
CuNaTe	4.38	7.11	1.623	Cu	Te	0.223	Na	0.666								
FeLiP*	3.691	6.023	1.632	Fe	P	0.24	Li	0.76	12	10	18	4 P, 4 Li, 4 Fe	4 Fe, 4 + 1 Li	4 Fe, 4 + 1 P		
MgNaSb	4.653	7.640	1.642	Mg	Sb	0.22429	Na	0.63839								
Fe ₂ As*	3.634	5.985	1.647	Fe(1)	As	0.265	Fe(2)	0.67	12	14	18	4 As, 4 Fe(1)	4 Fe(1), 1 + 4 Fe(2)	1 + 4 As		
BeLiAs*	3.749	6.219	1.659	Be	As	0.2217	Li	0.647	12	10	18	4 As	4 Be, 1 + 4 Li	1 + 4 As		
CuNaSe	4.10	6.82	1.663	Cu	Se	0.223	Na	0.651								
Mn ₂ As*	3.769	6.278	1.666	Mn(1)	As	0.265	Mn(2)	0.67	12	14	18	4 As, 4 Mn(1)	4 Mn(1), 1 + 4 Mn(2)	1 + 4 As		
BeLiP*	3.617	6.032	1.668	Be	P	0.219	Li	0.659	12	10	18	4 P, 4 Li	4 Be, 1 + 4 Li	1 + 4 P, 4 Be, 4 Li		
FeLi _{1.1} As*	3.776	6.349	1.681	Fe	As	0.24	Li	0.76	12	10	18	4 As, 4 Li	4 Fe, 4 Li	4 Fe, 4 As		
MnNaAs	4.206	7.077	1.683	Mn	As	0.213	Na	0.640								
MnNaP	4.086	6.884	1.685	Mn	P	0.205	Na	0.637								
ZnNaSb	4.44	7.49	1.687	Zn	Sb	0.221	Na	0.653								

MnNaSb	4.478	7.557	1.688	Mn	Sb	0.220	Na	0.651									
MgKSb	4.812	8.202	1.704	Mg	Sb	0.2001	K	0.6456									
MgBaGe*	4.64	7.92	1.707	Mg	Ge	0.205	Ba	0.661	12	10	18	4 Ge, 4 Mg, 4 Ba	4 Mg, 4 + 1 Ba	4 + 1 Ge, 4 Mg, 4 Ba			
MgBaSi	4.61	7.87	1.707	Mg	Si	0.206	Ba	0.661									
MnSrGe*	4.40	7.52	1.709	Mn	Ge	0.2056	Sr	0.6665	12	10	18	4 Ge, 4 Sr	4 Mn, 4 + 1 Sr	4 + 1 Ge, 4 Mn, 4 Sr			
MnCaGe*	4.23	7.27	1.719	Mn	Ge	0.2197	Ca	0.6616	12	10	18	4 Ge, 4 Ca	4 Mn, 4 + 1 Ca	4 + 1 Ge, 4 Mn, 4 Ca			
NiPdGe*	3.5952	6.2716	1.744	Ni	Ge	0.248	Pd	0.639	12	14	18	4 Ge, 4 Ni	4 Ni, 1 + 4 Pd	1 + 4 Ge			
MnBaGe*	4.50	7.92	1.760	Mn	Ge	0.1905	Ba	0.6680	12	10	18	4 Ge, 4 Ba	4 Mn, 4 Ba	4 Ge, 4 Mn, 8 Ba			
Cr ₂ As*	3.5923	6.3437	1.766	Cr(1)	As	0.275	Cr(2)	0.675	12	13	17	4 As, 4 Cr(1)	4 Cr(1), 1 + 4 Cr(2)	1 + 4 As			
MnKAs	4.391	7.791	1.774	Mn	As	0.188	K	0.644									
AlNaGe*	4.164	7.427	1.784	Al	Ge	0.217	Na	0.618	12	10	18	4 Ge, 4 Al	4 Al, 1 + 4 Na	1 + 4 Ge, 4 Na			
AlNaSi	4.135	7.379	1.785	Al	Si	0.223	Na	0.622									
MnKP	4.278	7.668	1.792	Mn	P	0.188	K	0.644									
VZrSi*	3.695	7.212	1.952	V	Si	0.255	Zr	0.640	12	9	17	4 Si, 4 V	4 V, 4 + 1 Zr	4 + 1 Si			
MX₂ and MX'X'' phases																	
GdO ₂	3.94	6.76	1.716	O(1)	Gd	0.182	O(2)	0.672									
UNTe	3.929	7.617	1.939	N	U	0.165	Te	0.624									
NdS ₂ *	4.022	8.031	1.997	S(1)	Nd	0.273	S(2)	0.636	12	13	17	4 Nd	9 S	1 + 4 Nd			
UBi ₂	4.445	8.908	2.004	Bi(1)	U	0.280	Bi(2)	0.637									
YbS _{1.7}	3.842	7.747	2.016	S(1)	Yb	0.24	S(2)	0.66									
CeTe ₂	4.52	9.12	2.018	Te(1)	Ce	0.27	Te(2)	0.625									
LaTe ₂	4.556	9.176	2.014	Te(1)	La	0.278	Te(2)	0.637									
LaTe ₂	4.507	9.128	2.025			0.27605		0.63314									
UP ₂ *	3.810	7.764	2.038	P(1)	U	0.280	P(2)	0.635	12	13	17	4 U	1 + 4 P(2), 4 P(1)	1 + 4 U			
UAsSb	4.152	8.463	2.038	Sb	U	0.295	As	0.641									
CmS ₂ *	3.926	8.01	2.040	S(1)	Cm	0.27	S(2)	0.63	12	13	17	4 Cm	1 + 4 S(2), 4 S(1)	1 + 4 Cm			
USb ₂	4.272	8.741	2.046	Sb(1)	U	0.280	Sb(2)	0.635									
Sm ₃₆ Se ₆₄ *	4.10	8.39	2.046	Se(1)	Sm	0.272	Se(2)	0.635	12	13	17	4 Sm	9 Se	4 + 1 Sm			

Table 1. (Continued)
MX₂ and MX'X'' phases

Phase	<i>a</i> (Å)	<i>c</i> (Å)	<i>c/a</i>	2(<i>a</i>)		2(<i>c</i> _I)		Wirkungsbereiche, no. of faces			Coordination polyhedron no. of close neighbours			
				atom		atom		site 2(<i>a</i>)	2(<i>c</i> _I)	2(<i>c</i> _{II})	site 2(<i>a</i>)	2(<i>c</i> _I)	2(<i>c</i> _{II})	
				atom	<i>z</i> _I	atom	<i>z</i> _{II}							
CmSe ₂	4.096	8.396	2.050	Se(1)	Cm	0.27	Se(2)	0.63						
UAs ₂	3.962	8.132	2.052	As(1)	U	0.280	As(2)	0.635						
ThBi ₂	4.492	9.298	2.070	Bi(1)	Th	0.28	Bi(2)	0.63						
Nd ₃₆ Te ₆₄	4.377	9.060	2.070	Te(1)	Nd	0.27087	Te(2)	0.63217						
AmTe ₂ *	4.358	9.027	2.071	Te(1)	Am	0.2699	Te(2)	0.6309	12	13	17	4 Te(1), 4 Am	5 Te(2), 4 Te(1)	4 + 1 Am
UPSe	3.951	8.185	2.072	P	U	0.2610	Se	0.6435						
USbSe	4.173	8.681	2.080	U	Sb	0.2885	Se	0.6315						
UPS	3.813	7.981	2.093	P	U	0.265	S	0.65						
USbTe	4.3185	9.0570	2.097	Te	U	0.2685	Sb	0.6289						
ThAs ₂	4.086	8.575	2.099	As(1)	Th	0.28	As(2)	0.64						
UAsSe*	3.981	8.371	2.103	As	U	0.2696	Se	0.6315	12	13	17	4 As, 4 U	5 Se + 4 As	4 + 1 U
UAsTe	4.167	8.764	2.103	As	U	0.25	Te	0.64						
UAsS*	3.874	8.158	2.106	As	U	0.2888	S	0.6334	12	13	17	4 As, 4 U	5 S + 4 As	1 + 4 U
ThSb ₂	4.353	9.172	2.107	Sb(1)	Th	0.275	Sb(2)	0.637						
U ₃₅ Te ₆₅	4.243	8.946	2.108	Te(1)	U	0.259	Te(2)	0.629						
USnTe	4.2596	9.1313	2.144	Sn	U	0.2734	Te	0.6287						
Zr ₃₆ As ₄₃ Se ₂₁	3.74	8.10	2.166	As	Zr	0.2647	(As + Se)	0.6210						
				(occ. 0.78)			(occ. 0.95)							

UGeS*	3.8112	8.3054	2.179	S	U	0.2888	Ge	0.632	12	13	17	4 U	4 + 1 Ge, 4 S	4 + 1 U
HfGeTe	3.87	8.502	2.196	Ge	Hf	0.241	Te	0.620						
HfGeS*	3.61	7.94	2.199	Ge	Hf	0.275	S	0.617	12	13	17	4 Ge, 4 Hf	4 + 1 S, 4 Ge	4 + 1 Hf
USiS*	3.767	8.285	2.199	S	U	0.284	Si	0.635	12	13	17	4 U	4 + 1 Si, 4 S	4 + 1 U
ZrGeS	3.626	8.019	2.212	Ge	Zr	0.276	S	0.622						
Zr ₃₉ As ₄₂ S ₁₉	3.62	8.04	2.221	As	Zr	0.2704	(As + S)	0.6206						
				(occ. 0.58)			(occ. 0.86)							
HfGeSe	3.69	8.20	2.222	Ge	Hf	0.267	Se	0.618						
ZrGeTe	3.866	8.599	2.224	Ge	Zr	0.249	Te	0.628						
ZrGeSe	3.706	8.271	2.232	Ge	Zr	0.263	Se	0.620						
TaSiAs	3.499	7.857	2.245	Si	Ta	0.256	As	0.609						
NbSiAs*	3.4908	7.8992	2.263	Si	Nb	0.2558	As	0.6117	12	13	17	4 Si, 4 Nb	4 Si, 4 + 1 As	4 + 1 Nb
HfSiS*	3.52	8.00	2.273	Si	Hf	0.269	S	0.615	12	13	17	4 Si, 4 Hf	4 + 1 S, 4 Si	4 + 1 Hf
ZrSiS	3.55	8.07	2.273	Si	Zr	0.271	S	0.622						
HfSiSe	3.63	8.32	2.292	Si	Hf	0.259	Se	0.615						
ZrSiTe	3.692	8.499	2.302	Si	Zr	0.225	Te	0.636						
Zr ₃₅ Si ₃₁ Se ₃₄ *	3.624	8.360	2.307	Si	Zr	0.2574	Se	0.6219	12	13	17	4 Si, 4 Zr	4 + 1 Se, 4 Si	4 + 1 Zr
HfSiTe*	3.67	9.73	2.651	Si	Hf	0.217	Te	0.645	12	13	17	4 Si, 4 Hf	4 Si, 4 Te	4 Hf

* Phases for which *Wirkungsbereiche* have been calculated

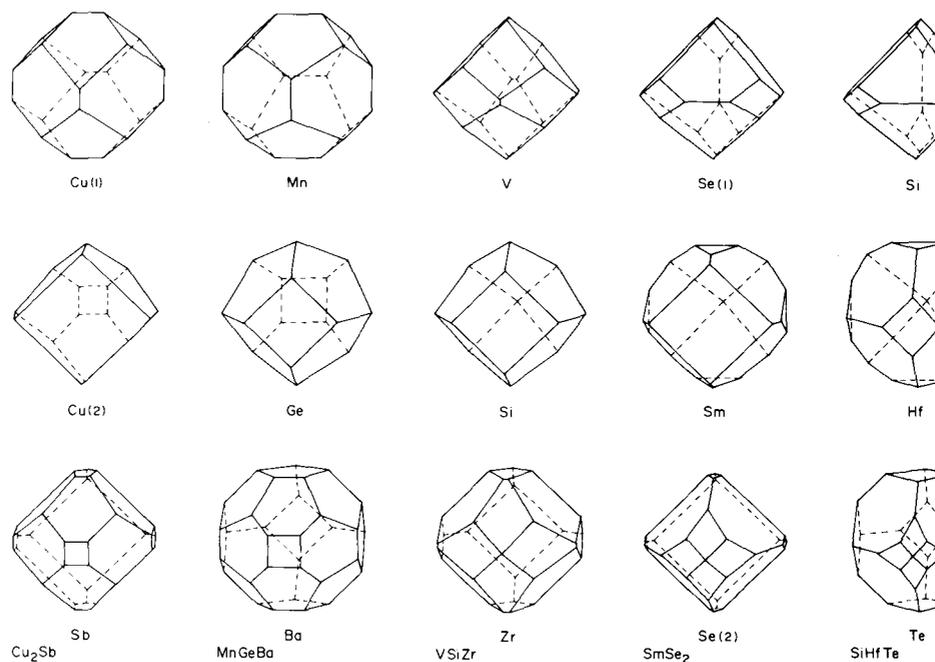


Fig. 3. *Wirkungsbereiche* surrounding the atoms in Cu_2Sb ($c/a=1.526$), MnGeBa ($c/a=1.760$), VSiZr ($c/a=1.952$), SmSe_2 ($c/a=2.046$) and SiHfTe ($c/a=2.651$) with the Cu_2Sb structure

site $2(c_{II})$ (MnAlGe excepted), whereas at larger axial ratios it is always the larger of the metal atoms that occupies $2(c_{II})$, with the exceptions noted above (see Table 1).

Comparison of Mn_2Sb and Mn_2As is interesting since in the former, Sb occupies $2(c_{II})$ whereas in the latter $\text{Mn}(2)$ does. Suppose $\text{Mn}(2)$ has a lower valency than $\text{Mn}(1)$ in these phases, and so is larger than $\text{Mn}(1)$. Secondly, suppose $\text{Mn}(2)$ has a valency of two, for example, then its diameter, $D_{\text{MnII}}=2.91 \text{ \AA}$. Accordingly in Mn_2Sb the largest atom, Sb , occupies $2(c_{II})$, whereas in Mn_2As as $\text{Mn}(2)$ is the largest atom it occupies $2(c_{II})$ in accord with observation and the above rule. Similarly for Fe_2As and Cr_2As if $\text{Fe}(2)$ and $\text{Cr}(2)$ have a lower valency than $\text{Fe}(1)$ and $\text{Cr}(1)$ and are larger than As , their observed presence on site $2(c_{II})$ is accounted for according to the above rule. Neutron diffraction studies show that in Mn_2Sb , Mn_2As and Cr_2As , $\text{Mn}(2)$ has a larger moment than $\text{Mn}(1)$ (Alperin et al., 1963; Wilkinson et al., 1957; Sirota and Ryzhkovskii, 1974; Yamaguchi et al., 1972) which indicates a lower valency and larger size for $\text{Mn}(2)$ than $\text{Mn}(1)$ according to Mori and Mitsui (1968), although Goodenough (1963) concludes the opposite*.

CuMgAs remains an anomaly; the *Wirkungsbereiche* leave no doubt that the largest atom, Mg , occupies site $2(c_1)$ (it matters not whether As has a

valency of three or five). Possibly the structure, which was reported in 1941, was incorrectly assigned.

Phases MX₂ and MX'X" have axial ratios greater than 2.0 with the exception of GdO₂ ($c/a = 1.716$) and UNTe ($c/a = 1.939$). z_{II} values are rather lower than those of M₂X phases ranging generally from 0.61 to 0.64 and z_I values are somewhat larger ranging generally from 0.25 to 0.29. The metal atom occupies the 2(c_I) position (except for USbSe where it is said to occupy 2(a)) and generally the X atom with the higher Group number occupies the 2(c_{II}) position, although some exceptions have been reported as in the structures of the UAsS (one report), USiS, UGeS and USbTe phases.

If $z_I = 0.25$ and $\bar{z}_{II} = 0.75$ and if $c/a = \sqrt{2}$, the Cu₂Sb structure would amount to a stack of face-sharing cubes along [001], with corners occupied by the 2(c_I) and 2(c_{II}) atoms, and the centres of alternate layers of cubes along [001] occupied by the 2(a) atoms. With $c/a > 1.414$ the cubes become tetragonal prisms; with $\bar{z}_{II} = z_I \neq 0.25$ the tetragonal prisms have different heights and with $\bar{z}_{II} \neq z_I \neq 0.25$, the "tetragonal prisms" also adopt irregular shapes. This is the state generally found in phases with the Cu₂Sb structure. No phases are reported with c/a as low as $\sqrt{2}$ and no phases are reported with $\bar{z}_{II} = z_I = 0.25$, but among phases with relatively low axial ratios, FeLiAs and FeLiP have been reported to have $\bar{z}_{II} = z_I$, and there is little difference between \bar{z}_{II} and z_I for MnZnSb ($c/a = 1.494$), MnAlGe ($c/a = 1.516$), Cu₂As ($c/a = 1.569$) and Mn₂Sb ($c/a = 1.608$).

Wirkungsbereiche

In such phases the atoms on site 2(a) are surrounded by a cubo-octahedron compressed along [001] (Fig. 2). Nevertheless since $c/2a < 1.0$, the *Wirkungsbereiche* resemble that of b.c. cubic structure (W $cI2$), except that there are no square faces normal to [001] (Fig. 3, see Cu(1)). When $c/2a \sim 1.0$, as for example in VZrSi, the *Wirkungsbereich* about V on 2(a) resembles that of the f.c. cubic structure (Cu $cF4$), with $c/a > 1.0$ (Fig. 3). The *Wirkungsbereiche* about atoms on site 2(a) always have 12 faces regardless of the axial ratio of the structure and the relative size of the atom that occupies the site.

The *Wirkungsbereich* about the atom that occupies 2(c_I) has 9 or 10 faces when the atom has a smaller diameter, and 13 or 14 faces when it has a larger diameter than the atom on 2(c_{II}), the only exceptions being NiPdGe and HfSiTe where the atoms have about the same size. The basic *Wirkungsbereich* with 10 faces has eight five-cornered faces and two four-cornered faces (one very large) normal to [001] (Fig. 3). The smaller four-cornered face may be

* Goodenough, however, assumes an ionic model, which may not be significant in the present context

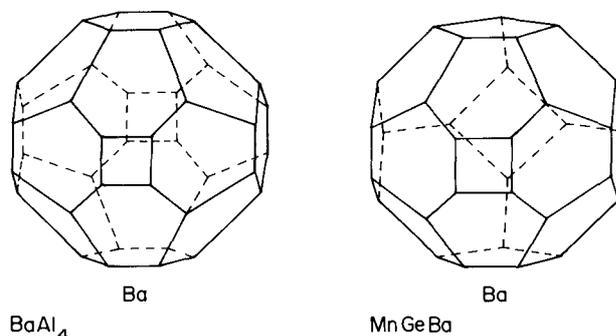


Fig. 4. *Wirkungsbereiche* about Ba in the BaAl_4 structure and about Ba in the MnGeBa phase with the Cu_2Sb structure

absent, giving rise to the *Wirkungsbereich* with 9 faces. Four triangular faces normal to $[100]$ and $[010]$ enter the *Wirkungsbereiche* for AsFe_2 , AsCr_2 and phases with axial ratios greater than 2.0, giving *Wirkungsbereiche* with either 13 or 14 faces depending on whether there are one or two faces normal to $[001]$ (Fig. 3).

The *Wirkungsbereich* about the atom on $2(c_{II})$ has 18 faces when there are two faces normal to $[001]$ at axial ratios less than about 1.8 and 17 faces when there is only one face normal to $[001]$ at larger axial ratios. The faces normal to $[100]$ and $[010]$ have five corners at axial ratios up to about 2.0 and four corners at larger axial ratios. These changes of shape with increasing axial ratio are shown in Fig. 3. The Te atom $2(c_{II})$ of HfSiTe is surrounded by a tetragonal prism of 4Hf and 4Te atoms, but is somewhat off-centre along $[001]$. This is reflected in the *Wirkungsbereich* about Te (Fig. 3), which is rather similar to that for the b.c. cubic structure.

Phases containing the large alkali or alkaline-earth elements accommodate them by an increase in the difference between z_1 and \bar{z}_{II} and by increases in both a and c , so that c/a values remain in the same range as those of other M_2X and $\text{M}'\text{M}''\text{X}$ phases. The *Wirkungsbereich* about Ba in MnBaGe is interesting to compare with that about Ba in BaAl_4 (Fig. 4). The Ge atom that lies within the tetragonal hexagon prism in MnBaGe, instead of outside like the capping atom Al(2) in BaAl_4 , removes the lower portion of the coordinating tetragonal hexagon prism (Fig. 2). Thus the faces normal to $[100]$ and $[010]$ which have six corners in BaAl_4 , have only five corners in MnBaGe; otherwise the *Wirkungsbereiche* are very similar.

Framework descriptions

Many framework descriptions of the Cu_2Sb , and La_2Sb (a superstructure of Cu_2Sb — see section 3 below) structures are possible particularly for

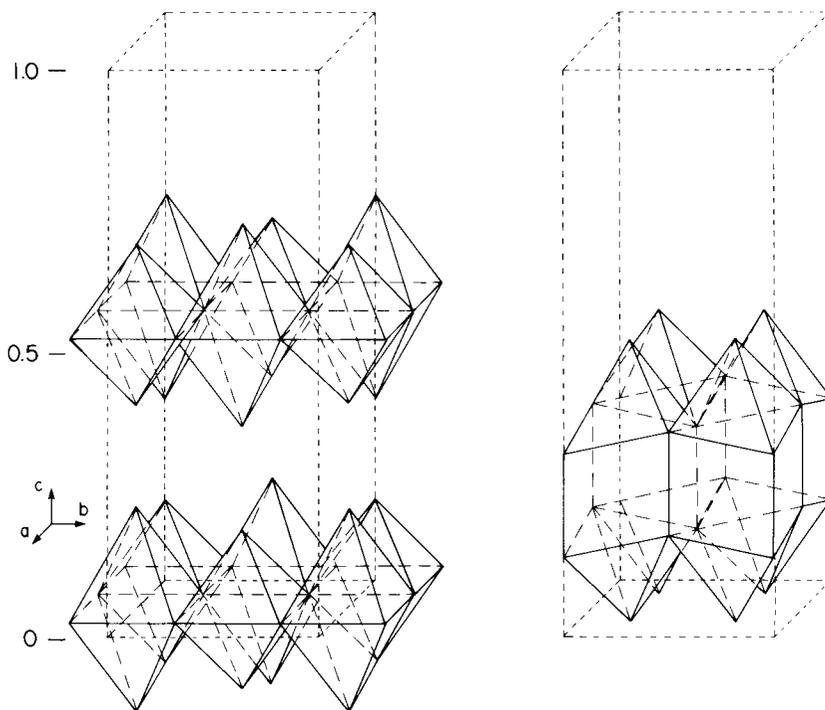


Fig. 5. Framework of distorted octahedra (left) and of dicapped distorted cubes (right) shown in the cell of the La_2Sb structure

phases with axial ratios less than about 1.80. Those based on slabs of edge-sharing octahedra and on slabs of face-sharing dicapped distorted cubes are indicated in Fig. 5 for the La_2Sb structure. Other descriptions can be based on the centred cubooctahedron (Fig. 2) or on the tetragonal hexagon prism that contains two atoms, also shown in Fig. 2. Descriptions based on the stacking of distorted graphite-like nets on (100) or (010) planes are also possible. The tetragonal hexagon prism is observed in several structures, for example it is found in the ThMn_{12} *I*128 structure and dicapped in the BaAl_4 *I*110 structure. In each of these, the prism is centred by a single atom; only in the Cu_2Sb , La_2Sb and Ca_2Sb structures is it found to contain two atoms displaced + and - from its centre.

The above framework descriptions become less and less realistic as c/a and the difference between z_1 and \bar{z}_1 increase. Indeed, for MX_2 and $\text{MX}'\text{X}''$ phases with $c/a > 2.0$ a framework description based on the cubic antiprism capped at one end along [001] by X'' , and shown for HfSiTe in Fig. 2, appears to be appropriate.

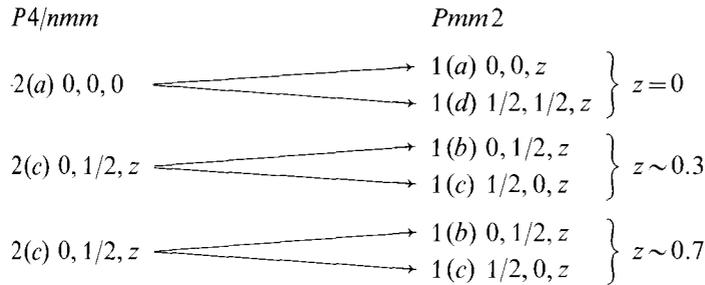
Table 2. Phases with the La_2Sb structure, with atomic parameters determined
 M_2X and $\text{M}'\text{M}''\text{X}$ phases

Phase	a (Å)	c (Å)	$c/2a$	Site 4(c) atom	4(e_1)		4(e_{II})		Wirkungsbereiche, no. of faces			Coordination polyhedron no. of close neighbours			
					atom	z_I	atom	z_{II}	site 4(c)	4(e_1)	4(e_{II})	site 4(c)	4(e_1)	4(e_{II})	
Ca_2As	4.63	15.56	1.680	Ca(1)	As	0.135	Ca(2)	0.328							
Ba_2As^*	5.13	17.36	1.692	Ba(1)	As	0.136	Ba(2)	0.325	12	9	17	4 As, 4 Ba(1), 4 Ba(2)	1 + 4 Ba(2), 4 Ba(1)	1 + 4 As, 4 Ba(1), 4 Ba(2)	
Sr_2Sb	5.002	17.405	1.740	Sr(1)	Sb	0.13666	Sr(2)	0.32825							
Ca_2Bi^*	4.72	16.54	1.752	Ca(1)	Bi	0.140	Ca(2)	0.334	12	9	17	4 Bi, 4 Ca(1), 4 Ca(2)	1 + 4 Ca(2), 4 Ca(1)	1 + 4 Bi, 4 Ca(1)	
Sr_2Bi	5.01	17.68	1.764	Sr(1)	Bi	0.138	Sr(2)	0.329							
Ba_2Sb	5.22	18.46	1.768	Ba(1)	Sb	0.136	Ba(2)	0.327							
Ba_2Bi	5.263	18.700	1.777	Ba(1)	Bi	0.13661	Ba(2)	0.32679							
ScCeSi	4.295	15.78	1.837	Sc	Si	0.124	Ce	0.326							
La_2Sb^*	4.629	18.098	1.955	La(1)	Sb	0.1377	La(2)	0.3203	12	9	17	4 La(1), 4 Sb	1 + 4 La(2), 4 La(1)	1 + 4 Sb	
$\text{MX}'\text{X}''$ phases															
UPTe^*	4.100	17.026	2.076	P	U	0.1145	Te	0.3095	12	14	17	4 U	4 P, 4 + 1 Te	4 + 1 U	
UAsTe	4.150	17.270	2.081	As	U	0.1199	Te	0.3122							
	4.148	17.256	2.080	As	U	0.1195	Te	0.3145							
UGeTe	4.1058	17.6014	2.143	Te	U	0.1230	Ge	0.3123							
UGeSe	3.9323	16.969	2.158	Se	U	0.1344	Ge	0.3135							
ThGeS^*	3.9411	17.1395	2.174	Ge	Th	0.1394	S	0.3113	12	13	17	4 Ge, 4 Th	4 + 1 S, 4 Ge	4 + 1 Th	

* Phases for which *Wirkungsbereiche* have been calculated

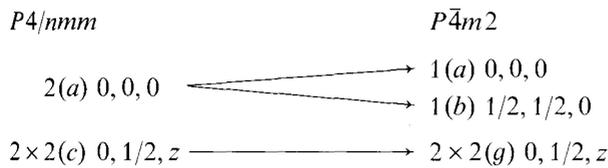
3. Structures derived from the Cu₂Sb type

A “splitted” form of the Cu₂Sb structure can be realized in *Pmm2* as follows:

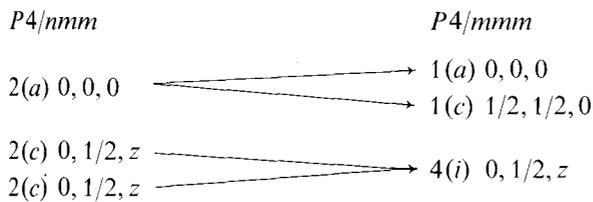


Although this structure is not known, its partially occupied form is in AgCuTe₂ *oP4* (*Pmm2*, Ag in 1(a) 0, 0, 0.962; Cu in 1(d) 1/2, 1/2, 0.039; Te(1) in 1(b) 0, 1/2, 0.720; Te(2) in 1(c) 1/2, 0, 0.279; *a* = 3.12, *b* = 4.05, *c* = 6.875 Å, 2*c*/(*a* + *b*) = 1.918). However, a difference of nearly 1 Å in the *a* and *b* edges of the cell is noted.

Partly splitted derivatives of the Cu₂Sb structure can be described in space groups *P4̄m2* and *P4̄*, e. g.



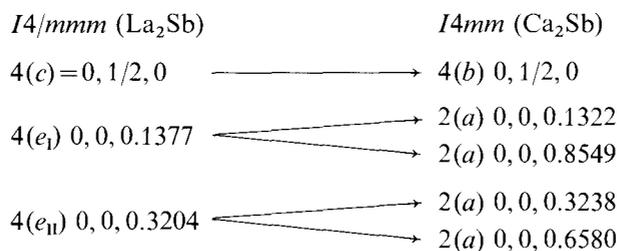
Although no representatives of this structure are known, a defect form in which site 1(*b*) is vacant, has been reported for Rh₃P₂ (El Ghadraoui et al., 1983). Partly “splitted” and partly “combined” structures can be found in space groups *P4/mmm*, *P4/mbm*, *P4̄2m*, *P422* and *P4/m*, e. g.



Although no representatives of these structures are known, a filled up form in which half of the cells in the layers of simple cubes are centred by As, is known in the AsTlPd₅ *tP7* structure adopted by very many phases (*P4/mmm*, Tl in 1(a) 0, 0, 0; Pd(1) in 1(c) 1/2, 1/2, 0; Pd(2) in 4(i) 0, 1/2, 0.30; As in 1(d)

$1/2, 1/2, 1/2$; $a = 4.005$, $c = 7.042 \text{ \AA}$, $c/a = 1.758$). Indeed, there are a number of other variants of the low-axial-ratio Cu_2Sb structure, as for example the $\text{AsLiMn } tP6$ structure ($P4/nmm$, Mn in $2(a) 0, 0, 0$; Li in $2(b) 0, 0, 1/2$; As in $2(c) 0, 1/2, z$ with $z = 0.758$; $a = 4.263$, $c = 6.179 \text{ \AA}$; $c/a = 1.449$ where similarly, alternate tetragonal prismatic subcells are centred successively along $[001]$, but the subcells in (001) slabs are alternately centred or empty, whereas they are either all centred or all empty in Cu_2Sb .

Finally, it is noted that the $\text{La}_2\text{Sb } tI12$ structure is a superstructure of Cu_2Sb with two cells stacked along $[001]$. The La_2Sb structure is described in $I4/mmm$ with La(1) in $4(c) 0, 1/2, 0$; Sb in $4(e_1) 0, 0, z$, with $z_1 = 0.1377$; La(2) in $4(e_{II})$ with $z_{II} = 0.3204$; $a = 4.626$, $c = 18.06 \text{ \AA}$ and $c/2a = 1.952$. The $\text{Ca}_2\text{Sb } tI12$ structure described in $I4mm$ is a partly splitted form of the La_2Sb structure with a similar size of cell ($c/2a = 1.747$):



M_2X , $\text{M}'\text{X}''\text{X}$ and $\text{MX}'\text{X}''$ phases with the La_2Sb structure follow similar rules for axial ratios, $c/2a$, $2z_1$ and $2z_{II}$ values as do phases with the Cu_2Sb structure. Thus M_2X phases have $c/2a$ values between about 1.7 and 1.8 except for (rare earth) $_2\text{X}$ phases which have $c/2a$ values of about 1.95. A metal atom occupies site $4(e_{II})$ with the larger coordination number and the X atom occupies $4(e_1)$. The splitted form Ca_2Sb behaves similarly to other M_2X phases. $\text{MX}'\text{X}''$ phases have $c/2a$ values in the range from 2.08 to 2.18 and the X atom from the higher group occupies site $4(e_{II})$ with the higher coordination number except for the UGeSe and UGeTe phases. The metal atoms occupy site $4(e_1)$; see Table 2.

The *Wirkungsbereiche* about the atoms on the three sites, with one exception, resemble those of phases with the Cu_2Sb structure and similar axial ratios as shown in Fig. 6. The *Wirkungsbereiche* about Ca(1), etc. of Ba_2As , Ca_2Bi and La_2Sb with $c/2a$ values from 1.692 to 1.955 are similar to that about V for VZrSi with the Cu_2Sb structure (Fig. 3). However those about P and Ge for UPTe and ThGeS with $c/2a$ greater than 2.0, differ from those about X of phases with the Cu_2Sb structure as shown in Figs. 3 and 6.

The doubly occupied tetragonal hexagon prismatic coordination polyhedron also occurs in the La_2Sb structure with $c/a < 2.0$ and in the Ca_2Sb structure.

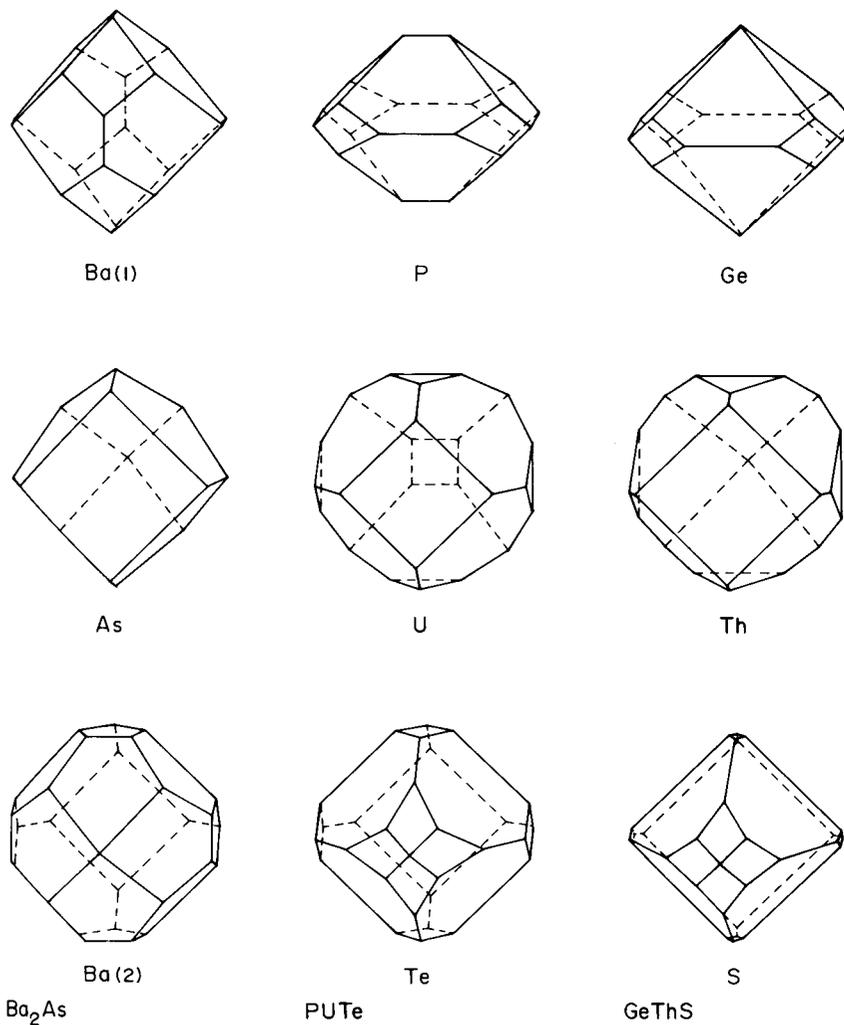


Fig. 6. *Wirkungsbereiche* surrounding the atoms in Ba₂As ($c/2a=1.692$), PUTe ($c/2a=2.076$) and GeThS ($c/2a=2.174$) with the La₂Sb type structure

4. Stability and availability

Since a single framework description cannot be applied sensibly to all phases with the Cu₂Sb structure, we may not expect to find a single principle that we can consider responsible for the stability and availability of the structure to all phases, as found for the BaAl₄ structure (Pearson, 1984). Certainly also, there are no overall valency or electron concentration rules that apply to all phases

with the structure. In such circumstances it may be profitable to compare apparent numbers of valency electrons required to satisfy the near-neighbour distances with those provided by the component atoms, using Pauling's (1947) equation: $R_{(1)} - R_{(n)} = 0.3 (\log n)$ where n equals valency divided by coordination number. Such calculations reveal two distinct situations. First, for the MX_2 and $\text{MX}'\text{X}''$ phases with $c/a > 2.0$, the apparent number of valency electrons required to satisfy the observed close-neighbour distances equals the number provided by the component atoms, generally to within one electron. Thus in these phases coordination and distances are such as to satisfy chemical bonding to the extent of the number of electrons provided by the atoms, but it should be noted that they differ from phases in which specific valency or electron-concentration rules are satisfied. Possibly they represent a type of metallurgical phase observed in other structures also, but so far not specifically characterized. Secondly, for $\text{M}'\text{M}''\text{X}$ phases that contain a large metal atom on site 2(c_{II}), the apparent number of valency electrons required by the close-neighbour distances, definitely exceeds those provided by the component atoms. This is a situation common to geometrical packing of large atoms within the voids of a particular framework, where the framework itself may satisfy specific chemical bonding between the atoms that compose it. Such is the case for most phases with the BaAl_4 structure (Pearson, 1984).

Finally, it is probably trivial to note that it is the versatility of site 2(c_{II}) that makes the structure available to atoms of a wide range of sizes. Perhaps less trivial is the question why the *Wirkungsbereich* always has 17 or 18 faces, no matter whether the atom it surrounds has a diameter of 2.5 or 4.5 Å!

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