

On the bindings in LiA_M phases

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(Received: July 1988)

Abstract

The LiA_M phases belong essentially to the Zintl phases ($\text{A}^{1-2}\text{A}_M^{9-17}$) since a large stability gap extends in LiA_M^{3-8} . (M is a mole number taking a value for each stable phase, A is a chemical element). The gap must be caused by a disharmony between the g correlations of the components. The set of g electrons is the union of peripheral d electrons (e band), of the energetically below lying and neighbouring sp electrons (c band), and of the sp or d or f electrons below c (f band). Since g is nearly non-occupied by Li -electrons the averaged occupancy of g may decrease down to values 0.25 in Li -rich phases. This means that there must be a harmonic but not congruent fit between g near Li , and g near A (hemstitch-fit). The special kind of fit appears to be a defining property of Zintl phases. The valence electrons are counted conventionally, and their correlation b must be as harmonic as possible to g to provide stability. This binding model for LiA_M phases explains Zalkin's rule (Li -rich phases are replacement-homeotypic to Li) by the harmonic fitting-in of the A atoms into the Li structure. The rule of Zintl (Li gives its b electron to A^n so that an A^{n+1} structure is formed by the A^n atoms) is explained by the essentially empty g correlation near Li , only the g electrons near A^n and the b electrons are of influence. The exceptions of Zintl's rule ($\text{LiTi}(\text{CsCl})$ e.g.) are a consequence of the g correlation site number rule requiring for heavy phases a decreased site number per atom. The uncommon compositions of various LiA_M phases are caused by g^1b harmonies.

Introduction

The data of two component phases containing Li (LiA_M phases) have been collected by 31Ewa, 58Han, 65Ell, 69Shu, 71Eck, 77Mof, 85Vil, 86Mas. They have been interpreted by 63Kle, 64Sch, 72Pea, 73Schä, 83Sch1 and these references may be consulted for earlier literature. Stability rules obeyed by LiA_M phases are for instance: The *spin compensation rule* of Lewis 1916 stating in present day terms that the spins occurring in the anionic component by Hund's rule are compensated by free spins of the cationic component (octet completion). The *supply rule* of Zintl 1932 (also 63Kle) takes the structure into consideration: The cationic component supplies m valence electrons to the anionic component A^n so that the component A^{n+m} forms a partial structure isotypic to the element A^{n+m} (example: $\text{LiAl}(\text{NaTi}$ type)). Zintl's rule may also be formulated (64Pea, 73Schä) as a generalization of Hume-Rothery's (1930) $8-n$ rule, stating that in a A^{10+n} element an atom has $8-n$ close distances to other atoms (another consequence of spin compensation). The rule of Zintl is so remarkable that $\text{A}^{1-2}\text{A}_M^{9-17}$ phases have been named Zintl phases. The *lacuna rule* of Bradley 1937 says

that the number of valence electrons per cell may be decreased by the formation of atomic lacunae. Unfortunately all rules have exceptions, so LiTi(CsCl) does not obey Zintl's rule (see also 75Fra). Therefore additional influences have to be sought and may be found in lattice-like spatial correlations of valence electrons and of core electrons (64,83,86Sch). Since Lewis' rule and, as shall be seen below, also Zintl's and Bradley's rules are closely related to spatial correlation of electrons, a plural correlations model will be compatible with the earlier valence rules. The model eventually will find additional stability rules (86Sch). One of these rules, the *electron rule*, says that not only the valence electrons (*b*) are of influence on stability but also the peripheral d electrons energetically below *b* (*e* band), furthermore sp electrons below *e* (*c* band) and finally, sp or d or f electrons below *e* (*f* band). The *e*, *c*, *f* bands generally form a collective correlation $e \sim c \sim f = g$, simplifying the determination of a bonding type (binding). Another rule is the *harmony rule* stating that the commensurability matrices describing the relation between the crystal cell *a* and for instance the cell *b* has preferentially integral elements. For more information on the model, and for related concepts and symbols see 83,86,88Sch.

Analysis

Li(W type, Struct.Rep.1.32), a (numbers of electrons=2,4)= $3.51\text{\AA}=b_B(1)=g_C(2)$, g -occupancy $N_{oc}(g)=0.75$. B is the body centered cubic Bravais type and C the primitive cubic type, (1)=(1,0,0;0,1,0;0,0,1), etc.

LiNa_M(no intermediate phase (nip), phase diagram 65Ell). The existence of two melts indicates that no energy decrease during formation occurs.

LiK_M(nip, phd 77Mof), two melts.

LiRb_M(nip, phd 58Han).

LiCs_M(nip, phd 58Han).

LiBe_M(nip, phd 77Mof).

LiMg_M(nip, phd 58Han), Li...Li_{0.3}Mg_{0.7}(W type).

Li₂Ca(MgZn₂,H4.8, drawing 64Sch.161, phd 65Ell), is a double replacement structure (64Sch) satisfying the volume relation $V(\text{Ca})=2V(\text{Li})$ and the valence electron relation $N_b(\text{Ca})=2N_b(\text{Li})$ just as MgCu₂ and TiBe₂(MgCu₂). $a(16,48,32)=H6.26;10.25\text{\AA}=b_{FH}^-(2;4.5/3)=g_{FH}^-(4;9/3)$, $N_{oc}(g)=0.67$. The compression (-) of the face centered cubic type in hexagonal aspect (F_H) might improve the spin compensation. The commensurability element 9/3 favours the +- stacking sequence (Zhdanov symbol) of the double layers LiCa₂+Li₃L (L=lacuna) following 84Sch.

Li₂₃Sr₆(Th₆Mg₂₃,F6.23,SR27.265,drw64Sch.156,phdSR27.267) exhibits a Li_{B1} site set with commensurability $a=a_{B1}(4)$ in which 36 of the 128 Li are replaced by 24 Sr. This replacement does not correspond to the volume ratio $V_{Sr}/V_{Li}=2.59$ because Li_{B1} is not a close packing. $a(140,376,240)=14.88\text{\AA}=b_B(4)=g_B(8)$, $N_{oc}(g)=0.74$. Comparison with the above binding of Li suggests that Sr serves to transform g_C of Li to g_B of Li₂₃Sr₆. Analogously as the Be-rich ABe_M phases are mostly close packings with (multiple) replacement, the Li-rich

LiA_M phases are W structures with replacement (rule of Zalkin, 57Zal). The analogy is continued in AB_M and AC_M phases.

Li_2Sr_3 (T8.12, SR27.266, drw ibid.) displays a site set htp to Sr_{B1} with $a = a_{\text{B1}}(2)$ in which 4Sr are replaced by 4 Li_2 , $a(32, 112, 120) = 9.63; 8.55\text{\AA} = g_{\text{B}}(\sqrt{32}; 5)$, $N_{\text{oc}}(g) = 0.83$.

LiSr_7 .h(U(0.5).(3.5), SR27.265, drw ibid.), $a(15, 58, 70) = 7.61; 6.50\text{\AA} = g_{\text{B}}(\sqrt{20}; 3.8)$, $N_{\text{oc}}(g) = 0.94$.

LiSr_8 .h(H(0.5).4, SR27.265), $a(9, 34, 40) = \text{H}4.31; 13.85\text{\AA} = g_{\text{BH}}(\sqrt{37}/3)$. B_{H} is the hexagonal aspect of B.

LiSr_8 .r(T1.6, SR27.265), $a(13, 50, 60) = 6.16; 8.86\text{\AA} = g_{\text{B}}(\sqrt{13}; 5)$, $N_{\text{oc}}(g) = 0.95$.

Li_4Ba (H24.6, SR30.25, drw ibid., phd65E11), $a(36, 96, 60) = \text{H}11.03; 8.89\text{\AA} = g_{\text{BH}}(4; 15/3)$.

LiSc_M , LiY_M , LiLa_M nip presumably. With these mixtures begins the set $\text{LiA}_M^{3d,n}$ forming a stability gap to be interpreted below.

LiTi_M (nip, phd77Mof), LiZr_M (nip, phd77Mof), LiHf_M (nip, phd77Mof).

LiV_M (nip, 69Shu), LiNb_M (nip, 69Shu), LiTa_M (nip, 69Shu).

LiCr_M (nip, 69Shu), LiMo_M (nip, 69Shu), LiW_M (nip, 69Shu).

LiMn_M (nip, 69Shu), LiTc_M , LiRe_M (nip? 58Han).

LiFe_M (nip, 69Shu), LiRu_3 (77Mof), LiOs_M . It will occur frequently that $\text{LiA}_M^{3d,n}$ does not form intermediate phases while $\text{LiA}_M^{4d,n}$ does. This is a consequence of the additional bonding of f electrons.

LiCo_M (nip, 58Han).

LiRh (H1.1, SR30.65) is htp Mg, but the components are not arranged as in AuCd_r (O2.2, SR2.11, drw64Sch.114), rather layers parallel to a_1, a_2 are filled by alternating components. This indicates a certain attraction of atoms of the same kind the cause of which will become apparent now. $a(1, 11, 8, 10) = \text{H}2.65; 4.36\text{\AA} = g_{\text{BH}}(2; 15/3)$. LiRh is thus homeodesmic to $\text{Ru}(\text{Mg})$ (88Sch), but the occupancy is strikingly low, $N_{\text{oc}}(g) = 0.50$. A g_{CH} correlation cannot be assumed since it would cause a $++--$ stacking following 84Sch. In the neighbourhood of the Li atoms there must exist a correlation $a = g_{\text{BH}}^*(1; 7.5/3)$ being commensurate with g_{BH} . This remarkable circumstance may be compared with a hemstitch where a large-mesh tissue is neighbouring harmonically to a small-mesh tissue.

LiRh_3 (LiIr_3 , P1.3, SR42.143) is htp Mg once more, but the components are not arranged as in Ni_3Sn (H6.3, drw64Sch.114), rather the minority atoms are connected in rows along a_1 causing the orthorhombicity and leaving layers parallel to a_1, a_3 containing Rh only. $a(2, 58, 48, 60) = 2.66; 8.60; 4.66\text{\AA} = g_{\text{BH}}(2; 30/3)$, $N_{\text{oc}}(g) = 0.70$. The binding is written for the hexagonal subcell and says that LiRh and LiRh_3 are isodesmic. It is seen that $N_{\text{oc}}(g)$ depends approximately linearly on the mole fraction N_{Rh} , so that the binding is grossly spoken, only occupied by the electrons of Rh. This must be considered as the energetic fundament of Zintl's rule, leaving only b electrons, and g electrons of A, for the binding of LiA . Numerous bindings below confirm this assumption. Furthermore the above mentioned stability gap of Li compounds must be considered as a consequence of the electron distances not allowing a hemstitch fit of the correlations.

- LiIr(LiRh,SR42.142), $a(1,11,8,14)=H2.65;4.40\text{\AA}=g_{BH}(2;15/3)$, $N_{oc}(g)=0.57$.
 LiIr₃(P1.3.LiRh₃,SR42.98), $a(2,58,48,84)=2.67;8.70;4.67\text{\AA}=g_{BH}(2;30/3)$.
 LiNi_M(nip, 77Mof).
 Li₅Pd(F,76Vuc,phd77Mof), $a=19.2\text{\AA}$. A test for isotypism with Li₂₂Pb₅ was not satisfactory.
 Li₁₅Pd₄(Cu₁₅Si₄,B30.8,SR44.118,drw64Sch.226), $a(60,280,128,160)=10.68\text{\AA}=b_F(2.5)=g_B(10)$. The g occupancy is only $N_{oc}(g)=0.31$ because of the low Pd content. For b appears also possible $a=b_C(4)$.
 Li₃Pd.h(Fe₃Si₃F3.1,SR42.143,drw64Sch.127), $a(12,64,32,40)=6.19\text{\AA}=b_B(2)=g_B(6)$, $N_{oc}(g)=0.34$. Since one b electron must be exited from Pd, the phase becomes unstable at lower temperatures.
 Li₂Pd(AlB₂,H1.2,SR42.143,44.118), $a(2,14,8,10)=H4.23;2.73\text{\AA}=b_{BH}(1;3/3)=g_{BH}(3;9/3)$, $N_{oc}(g)=0.42$.
 Li_{1,2}Pd_{0,8}h(CsCl,SR44.118), $a(1,10,6,8)=2.98\text{\AA}=b_B(1)=g_B(3)$, $N_{oc}(g)=0.46$. b electrons are thermally excited so that the phase is stable only at elevated temperatures.
 LiPd(LiRh,SR42.143,44.118), $a(1,12,8,10)=H2.77;4.20\text{\AA}=b_H(1;1.5)=g_{BH}(2;15/3)$, $N_{oc}(g)=0.52$.
 LiPd₂(H,SR42.143), or rather LiPd₃(84Wid), $a=H3.84;4.34\text{\AA}$.
 Li_{1,1}Pd_{2,9}(M2.6,SR45.93), $a(2,64,48,60)=5.41;2.73;7.67\text{\AA}=b_C(\sqrt{2};1/\sqrt{2};2)=g_B(\sqrt{32};\sqrt{8};8)$, $N_{oc}(g)=0.68$.
 LiPd₇(MgPt₇,F1.7,SR42.143,44.118,drwSR27.323) cmp 1500°C. $a(4,288,224,280)=7.66\text{\AA}=b_F(1)=g_B(8)$, $N_{oc}(g)=0.78$. Instead of $a=b_F(1)$ also $a=b_C(2)$ may be assumed to account for the paramagnetic susceptibility (77Loe).
 Li₂Pt(AlB₂,SR41.131), $a(2,14,8,14)=H4.19;2.66\text{\AA}=b_{BH}(1;3/3)=g_{BH}(3;9/3)$, $N_{oc}(g)=0.47$.
 LiPt(LiRh,SR41.131), $a(1,12,8,14)=H2.73;4.23\text{\AA}=b_H(1;1.5)=g_{BH}(2;15/3)$, $N_{oc}(g)=0.58$.
 LiPt₂(MgCu₂,F2.4,71Eck), $a(8,176,128,224)=7.60\text{\AA}$ is improbable since volume relation is not fulfilled, see LiPt₇.
 LiPt₇(MgPt₇,SR27.323), $a(4,288,224,392)=7.76\text{\AA}=b_F(1)=g_B(8)$, $N_{oc}(g)=0.89$.
 LiCu_M(nip, 65Ell).
 Li₉Ag(C,SR18.209, phd58Han).
 Li₄Ag(htp Cu₅Zn₈,SR18.208), $a(52,184,80,100)=9.70\text{\AA}=b_B(3)=g_B(9)$, $N_{oc}(g)=0.29$. The homeotypism is more formal since there is a large difference of the binding to that of brass.
 Li₉Ag₃(Cu₅Zn₈,SR38.119,drw64Sch.132), $a(52,232,128,160)=9.60\text{\AA}=g_B(9)$, $N_{oc}(g)=0.39$. This structure determination was based on powder diffractometer data, and requires confirmation by single crystal diffraction.
 Li_{1,1}Ag_{0,9}(CsCl,SR18.208), $a(2,12,8,10)=3.17\text{\AA}=b_B(1)=g_B(3)$, $N_{oc}(g)=0.59$. The Li_mAg marginal phase goes up to Li₄₅Ag₅₅, $a(4,26,18,22)=g_B(4)=g_B^*(2)$, $N_{oc}(g)=0.54$.
 Li₁₅Au₄(Cu₁₅Si₄Li₁₅Pd₄,SR26.157,phd ibid.), $a(76,280,128,224)=10.83\text{\AA}=b_F(2.5;6/2)=g_B(10)$, $N_{oc}(g)=0.35$.
 Li₃Au(Fe₃Si₃F3.1,Li₃Pd.h,SR26.157), $a(16,64,32,56)=6.30\text{\AA}=b_B(2)=g_B(6)$, $N_{oc}(g)=0.39$.

- Li₂Au.h(61Kie).
 Li_{5/6}Au_{3/4}.r(H6.3,SR26.158), $a(9,45,27,47)=H7.23;2.77\text{\AA}=b_{\text{H}}(\sqrt{25/3};1.1)=g_{\text{BH}}(5;9/3)$,
 $N_{\text{oc}}(g)=0.57$.
 Li₅₆Au₄₄(CsCl,SR26.158), $a(2,11.0,7.0,12.3)=3.10\text{\AA}=b_{\text{B}}(1)=g_{\text{B}}(3)$, $N_{\text{oc}}(g)=0.59$.
 Li₅₄Au₄₆(T1.1,SR26.158), $a(2,11.2,7.2,12.6)=3.23;2.83\text{\AA}=g_{\text{B}}(\sqrt{10};2.75)$, $N_{\text{oc}}(g)=0.60$.
 LiAu(O1.1,SR26.158), $a(2,12.8,14)=3.30;3.21;2.80\text{\AA}$, analysis is postponed.
 Li₄Au₅.h(H,SR26.158).
 Li₂Au₃(complex powderdiag., 61Kie).
 LiAu₃.m(shear htp Cu₃Au,SR26.158), $a=3.96;4.02\text{\AA}=g_{\text{B}}(4;4.5)$, tentative, $N_{\text{oc}}(g)=0.71$.
 The elaboration of this structure appears desirable.
 LiAu₃.r(Cu₃Au,SR26.158), $a(4,32,24,42)=3.97\text{\AA}=b_{\text{F}}(1)=g_{\text{B}}(4)$, $N_{\text{oc}}(g)=0.80$. The Cu₃Au isotope list stable since it provides an improved commensurability as compared with Au(Cu, SR1.38), $a(4,40,32,56)=4.08\text{\AA}=b_{\text{F}}(1)=e_{\text{B}}(\sqrt{8};2.5)=g_{\text{U}}(4;5)$.
 LiZn(NaTl,F2.2,SR3.256,drw64Sch.127,phd58Han) is a replacement-htp of Li with the commensurability $a=a_{\text{Li}}(2)$. The heterotypism to Li₅₆Au₄₄(CsCl) signalizes a heterodesmism to this phase. $a(24,96,64,64)=6.22\text{\AA}=b_{\text{C}}(\sqrt{8};3)=g_{\text{C}}(8)$, $N_{\text{oc}}(g)=0.48$. The earlier assumed binding (83Sch1) $a=b_{\text{F}}(2)=e_{\text{B}}(4)$ is implied in $a=g_{\text{C}}(8)$. The binding will be more harmonic in LiGa(NaTl), but partial harmony may be sufficient for stability. The heterodesmism LiZn-LiAu obeys the site number rule (83Sch).
 It would be interesting to know the structures of the following phases,
 Li₂Zn₃.h,
 Li₂Zn₃.r,
 LiZn₂,
 Li₂Zn₅.h,
 Li₂Zn₅.r(H(0.8).2,SR3.634), $a(\dots)=H4.36;2.51\text{\AA}$, needs further work.
 LiZn₄.h,
 LiZn₄.r(Mg,SR3.634), $a(3.6,17,13,13)=H2.79;4.39\text{\AA}=b_{\text{CH}}(1;3.8/3)=g_{\text{B}}(2;15/3)$.
 Li₃Cd(Cu,SR3.636, phd 58Han), $a(5,16,8,10)=4.26\text{\AA}=b_{\text{F}}(1.25)=g_{\text{C}}(5)$, $N_{\text{oc}}(g)=0.31$.
 LiCd(NaTl,SR3.636) cmp, $a(24,96,64,80)=6.70\text{\AA}=b_{\text{C}}(\sqrt{8};3)=g_{\text{C}}(8)$, $N_{\text{oc}}(g)=0.52$.
 LiCd₃.h,
 LiCd₃.r(Mg,SR3.636), $a(3.5,16,12,15)=H3.09;4.90\text{\AA}=b_{\text{CH}}(1;3.8/3)=g_{\text{BH}}(2;15/3)$,
 $N_{\text{oc}}(g)=0.78$.
 Li₆Hg(phd 58Han)
 Li₃Hg(Fe₃Si, Li₃Pd.h,SR3.633), $a(20,64,32,56)=6.60\text{\AA}=b_{\text{HT}}(\sqrt{36/5};3/2)=g_{\text{B}}(6)$, $N_{\text{oc}}(g)=0.40$. It may be assumed that the presence of Li increases the b contribution of Hg.
 Li₂Hg.
 LiHg(CsCl,SR3.265) cmp 595°C. $a(3,12,8,14)=3.29\text{\AA}=b_{\text{C}}(1.5)=g_{\text{B}}(3)$, $N_{\text{oc}}(g)=0.69$. The homeotypism LiCd(NaTl)-LiHg(CsCl) obeys the site number rule (83,86Sch).
 LiHg₂.
 LiHg₃(Ni₃Sn,SR3.632), $a(14,64,48,84)=H6.25;4.80\text{\AA}=g_{\text{BH}}(4;15/3)$, $N_{\text{oc}}(g)=0.88$.

Li_3Al_3 (N9.4, SR33.6, drw ibid., phd58Han) is a replacement-htp of W. There are Al_∞ zig-zag chains in the direction of the shortest axis with neighbouring atoms. The chains are neighbouring as in Li_2Ga , but there is still an additional shear. Binding analysis is postponed.

$\text{Li}_3\text{Al}_2(\text{Bi}_2\text{Te}_3, \text{R3.2, SR39.5})$ is only topologically isotypic to Bi_3Te_3 , metrically Bi_3Te_3 is htp to NaCl, and Li_3Al_2 to CsCl. $a(27,66,12)=\text{H}4.51; 14.26\text{\AA}=b_{\text{FH}}(2;7.6/3)=g_{\text{BH}}(2;31/3)$, $N_{\text{oc}}(g)=0.85$.

$\text{LiAl}(\text{NaTi}, \text{LiZn}, \text{SR3.266})$ cmp, $a(32,80,16)=6.38\text{\AA}=b_{\text{F}}(2)=g_{\text{B}}(4)$. A completion to a g_{C} correlation as in LiZn is not necessary since f electrons are not involved.

Li_2Al_3 (see 73Schä).

$\text{Li}_2\text{Ga}(\text{ZrSi}_2, \text{Q2.4, SR44.62, drw64Sch.92, phd77Mof})$ is htp W while ZrSi_2 is htp Cu, it contains 6 atom layers parallel to a_1, a_3 , $a(20,56,32,32)=4.56; 9.54; 4.36\text{\AA}=b_{\text{HT}}(2;5/2)=g_{\text{C}}(\sqrt{32};12)$, $N_{\text{oc}}(g)=0.36$. The g_{C} correlation exists near Ga while near Li the above g_{B} is valid.

$\text{Li}_3\text{Ga}_2(\text{Bi}_2\text{Te}_3, \text{Li}_3\text{Al}_2, \text{SR44.62, drwSR48.56})$, $a(27,78,48,48)=\text{H}4.38; 13.90\text{\AA}=b_{\text{FH}}(2;7.6/3)=g_{\text{CH}}(4;31/3)$, $N_{\text{oc}}(g)=0.41$. It may be assumed that b_{FH} is not fully commensurate to g .

Li_3Ga_4 (H5.4, SR48.56, drw ibid.), $a(17,50,32,32)=\text{H}4.38; 8.26\text{\AA}=b_{\text{FH}}(2;4.25/3)=g_{\text{CH}}(4;17/3)$, $N_{\text{oc}}(g)=0.45$.

$\text{LiGa}(\text{NaTi}, \text{LiZn}, \text{SR3.267, drwSR48.56})$ cmp 740°C , $a(32,96,64,64)=6.21\text{\AA}=b_{\text{F}}(2)=g_{\text{C}}(8)$, $N_{\text{oc}}(g)=0.50$. The binding could also be interpreted as $a=g_{\text{F}}(4)$, but this proposal does not hold in $\text{LiIn}(\text{NaTi})$.

LiGa_2 (phd 77Mof).

$\text{Li}_3\text{Ga}_{14}$ (R3.14, 82Stö) does not obey Zalkins rule, it contains Ga clusters. $a(135,438,336,336)=\text{H}8.46; 16.85\text{\AA}=g_{\text{CH}}(\sqrt{57};36/3)$, $N_{\text{oc}}(g)=0.61$. This binding must be tentative since the structure of LiGa_2 is still unknown.

$\text{Li}_{12}\text{In.h}$ (phd77Mof, earlier results 70Thü).

$\text{Li}_6\text{In.h}$.

$\text{Li}_4\text{In.h}$.

$\text{Li}_{13}\text{In}_3$ (F26.6, SR45.81) replacement htp W, $a=a_{\text{Li}}(4)$, $a(176,448,192,240)=13.56\text{\AA}=b_{\text{C}}(\sqrt{32};5.6)=g_{\text{C}}(16)$, $N_{\text{oc}}(g)=0.26$.

Li_3In .

$\text{Li}_{11}\text{In}_4.h$.

$\text{Li}_{73}\text{In}_{27}.h$.

Li_8In_3 .

$\text{Li}_5\text{In}_2.h$.

$\text{Li}_2\text{In}(\text{ZrSi}_2, \text{Li}_2\text{Ga}, \text{SR45.81})$, $a(20,56,32,40)=4.76; 10.02; 4.74\text{\AA}=b_{\text{HT}}(2;5/2)=g_{\text{C}}(\sqrt{32};12)$, $N_{\text{oc}}(g)=0.39$.

Li_7In_4 .

$\text{Li}_3\text{In}_2(\text{Bi}_2\text{Te}_3, \text{Li}_3\text{Al}_2, \text{SR45.80})$, $a(27,78,48,60)=\text{H}4.75; 14.74\text{\AA}=b_{\text{FH}}(2;7.6/3)=g_{\text{CH}}(4;30/3)$.

$\text{Li}_5\text{In}_4(\text{Li}_5\text{Ga}_4, 85\text{Vil})$, $a(17,50,32,40)=\text{H}4.78; 8.88\text{\AA}=b_{\text{FH}}(2;4.5/3)=g_{\text{CH}}(4;18/3)$.

$\text{LiIn}(\text{NaTi}, \text{LiZn}, \text{SR}3.267)$, $a(32,96,64,80)=6.80\text{\AA}=b_{\text{F}}(2)=g_{\text{C}}(8)$, $N_{\text{oc}}(g)=0.53$.

$\text{Li}_{22}\text{Ti}_5(\text{Li}_{22}\text{Pb}_5, \text{F}88.20, 85\text{Vil}, \text{drw}64\text{Sch}.224, 73\text{Sch}\ddot{a}, \text{phd}58\text{Han})$ is replacement htp Li with $a=a_{\text{Li}}(6)$. $a(592, 1504, 640, 1120)=20.00\text{\AA}=b_{\text{FU}}(8;10/2)=g_{\text{C}}(24)$, $N_{\text{oc}}(g)=0.28$. The phase is with respect to g isodesmic to Li_3Ti . The b correlation requires only the commensurability $a=a_{\text{Li}}(3)$, but the misfit in a_3 direction generates electro-dipoles which favour $a=a_{\text{Li}}(6)$. F_{U} is the tetragonal bodycentered aspect of F .

$\text{Li}_3\text{Ti}(\text{Fe}_3\text{Si}, \text{Li}_3\text{Pd}, \text{h}, \text{SR}45.80)$, $a(24, 64, 32, 56)=6.67\text{\AA}=b_{\text{C}}(\sqrt{8;3})=g_{\text{C}}(8)$, $N_{\text{oc}}(g)=0.34$. Here it must be assumed that b breaks in one direction out of g .

$\text{Li}_5\text{Ti}_2(\text{Li}_5\text{Sn}_2, \text{R}5.2, \text{SR}45.80)$, $a(33, 90, 48, 84)=\text{H}4.72; 20.40\text{\AA}=b_{\text{H}}(2;8.5)=g_{\text{CH}}(4;42/3)$, $N_{\text{oc}}(g)=0.38$.

$\text{Li}_2\text{Ti}(\text{ZrSi}_2, \text{Li}_2\text{Ga}, 85\text{Vil})$, $a(20, 56, 32, 56)=4.74; 10.02; 4.79\text{\AA}=b_{\text{C}}(\sqrt{4.5;4.5})=g_{\text{B}}(\sqrt{18;9})$, $N_{\text{oc}}(g)=0.51$. The change $g_{\text{C}} \rightarrow g_{\text{B}}$ may have to do with the low melting point of Li_2Ti and LiTi as compared with Li_3Ti .

$\text{LiTi}(\text{CsCl}, \text{SR}3.268)$ cmp, $a(4, 12, 8, 14)=3.43\text{\AA}=b_{\text{FU}}(1.5;2/2)=g_{\text{B}}(3)$, $N_{\text{oc}}(g)=0.70$. The $N_{\text{oc}}(g)$ value does not well extrapolate from the smaller values, a similar break occurs in the liquidus line. The $N_{\text{oc}}(g)$ value 0.70, being higher than the value 0.53 in LiIn , indicates the decrease of the g site number per atom being 32 in LiIn and 27 in LiTi . This decrease, caused by the f electrons, is in accordance with the site number rule.

$\text{Li}_{21}\text{Si}_5$ (htp $\text{Li}_{22}\text{Pb}_5, \text{Li}_{22}\text{Ti}_5, \text{SR}31.48, 87\text{Nes}, \text{phd}65\text{Eil}, 69\text{Shu}$), $a(672, 1344, 160)=18.71\text{\AA}=b_{\text{FU}}(8;11/2)=g_{\text{B}}(12)$. It is heterodesmic to Cu_5Zn_8 yielding $a=b_{\text{B}}(3.5)=e_{\text{B}}(7)$.

$\text{Li}_4\text{Si}(\text{O}, 71\text{Eck})$.

" $\text{Li}_7\text{Si}_2(\text{O}, \text{SR}30.66)$ " is really $\text{Li}_{13}\text{Si}_4$ (SR41.87).

$\text{Li}_{10}\text{Si}_3$ (F80.24, SR30.152) is perhaps one phase with $\text{Li}_{21}\text{Si}_5$, $a(704, 1408, 192)=18.61\text{\AA}=b_{\text{FU}}(\sqrt{72;10/2})=g_{\text{B}}(12)$, $N_{\text{oc}}(g)=0.67$.

$\text{Li}_{13}\text{Si}_4$ (O26.8, SR41.87, drw75Mül.52, 82), $a(58, 116, 16)=7.99; 15.21; 4.43\text{\AA}=b_{\text{H}}(2;7)=g_{\text{BH}}(2;35)$.

$\text{Li}_{14}\text{Si}_6$ (R(4.7).2, SR46.97) cmp, lacuna htp Li_5Sn_2 , $a(38, 76)=\text{H}4.44; 18.13\text{\AA}=b_{\text{FH}}(2;10/3)=g_{\text{BH}}(2;40/3)$, $N_{\text{oc}}(g)=0.74$.

" $\text{Li}_2\text{Si}(\text{N}8.4, \text{SR}30.65)$ " is really $\text{Li}_{14}\text{Si}_6$ (SR46.97).

Li_2Si_2 (O96.56, SR48.74) contains Si_5 rings and Si_4 stars. $a(320, 640, 112)=8.61; 19.74; 14.34\text{\AA}=b_{\text{FH}}(4;11/3)=g_{\text{BH}}(4;45/3)$.

$\text{Li}_{22}\text{Ge}_5(\text{Li}_{22}\text{Pb}_5, \text{Li}_{22}\text{Ti}_5, \text{SR}29.118, \text{phd}77\text{Mof})$, $a(672, 1504, 640, 640)=18.86\text{\AA}=b_{\text{FU}}(8; 11/2)=g_{\text{C}}(24)$, $N_{\text{oc}}(g)=0.25$. The b correlation must be twinned in a .

$\text{Li}_{15}\text{Ge}_4(\text{Cu}_{15}\text{Si}_4, \text{Li}_{15}\text{Pd}_4, \text{SR}30.53)$, $a(124, 280, 128, 128)=10.78\text{\AA}=b_{\text{C}}(5)=g_{\text{B}}(10)$, $N_{\text{oc}}(g)=0.33$. The b correlation showed in $\text{Li}_{15}\text{Au}_4$ an apparently lower occupation because of the easy contribution of $\text{Au}5d$ electrons.

Li_iGe_2 (Q14.4, SR41.70, drw73Schä, 75Mül.29) is replacement-htp Li, with $a=a_{\text{Li}}(3;3\sqrt{2}; \sqrt{2})$, the Ge are not distributed as in Fe_3Si , rather some Ge form pairs in a_1 direction. $a(60, 136, 64, 64)=9.24; 13.21; 4.63\text{\AA}=b_{\text{F}}(2.5;3\sqrt{2};\sqrt{2})=g_{\text{C}}(12;12;2;4\sqrt{2})$, $N_{\text{oc}}(g)=0.28$. The compres-

sion of a_1 as compared with a_3 must be related to the Ge-pairs.

Li_3Ge (77Mof) is said to have in $\text{LiGe}_{0.1}$ a maximum melting point. Since 75Mül does not mention it, it must be assumed to be really Li_7Ge_2 .

Li_9Ge_4 (Q18.8,SR35.64,drw75Mül.87) is a quasihexagonal, replacement- and lacuna-htp of Li, all Ge are united to pairs in a_3 direction and the lacunae are in the neighbourhood of pairs. The pair formation indicates an attraction of Ge by the g electrons and the increased b concentration near the Ge_2 causes the lacunae. $a(100,232,128,128)=4.49;7.87;24.44\text{Å}=b_{\text{FH}}(2;13.5/3)=g_{\text{CH}}(4;54/3)$.

$\text{Li}_{11}\text{Ge}_6$ (Q22.12,SR41.69,drw75Mül.43) the association of Ge forms now Ge_3 rings with normal a_1 . $a(140,328,192,192)=4.38;24.55;10.64\text{Å}=b_{\text{FH}}(2;14/3;5.5/2)=g_{\text{CH}}(4;54/3;11/2)$. The proposal can only be a trial because of the large a cell.

$\text{Li}_{1.7}\text{Ge}$ (P23.14,85Vil,drw75Mül.35,36) htp $\text{Li}_{11}\text{Ge}_6$. $a=4.36;14.52;20.02\text{Å}$. Binding analysis is postponed.

$\text{LiGe}(\text{MgGa},\text{U}8.8,\text{SR}41.115,\text{drw}72\text{Pea}.768)$ is displacive-homeotypic to NaCl with $a=a_{\text{NaCl}}(2;1)$. $a(80,192,128,128)=9.75;5.78\text{Å}=b_{\text{F}}(\sqrt{10};4/2)=g_{\text{C}}(\sqrt{160};7)$. $N_{\text{oc}}(g)=0.47$. The root indicates a finite rotation of the binding around a_3 and this must be considered as a cause of the displacive homeotypism $\text{LiGe}-\text{NaCl}$. The increase of the b concentration and the approximate conservation of the binding of $\text{LiGa}(\text{NaTl})$ causes a strong decrease of $N_{\text{oc}}(g)$, so that LiSn cannot be isotypic to LiGe .

$\text{Li}_{22}\text{Sn}_5$ ($\text{Li}_{22}\text{Pb}_5$,F88.20, $\text{Li}_{22}\text{Tl}_5$,SR29.122,drw75Mül.65,phd58Han), $a(672,1504,640,800)=19.78\text{Å}=b_{\text{FU}}(8;11/2)=g_{\text{C}}(24)$, $N_{\text{oc}}(g)=0.26$. The twinning of b_{FU} suggests to seek a tetragonal low temperature phase.

Li_7Sn_2 (Li_7Ge_2 ,Q14.4,SR41.88,drw75Mül.29) cmp, $a(60,136,64,80)=9.80;13.80;4.75\text{Å}=b_{\text{F}}(2.5;3\sqrt{2};\sqrt{2})=g_{\text{C}}(12;12\sqrt{2};4\sqrt{2})$. The Sn are partly associated to pairs along $a_1=3a_{\text{Li}}$. A rule for d_{Sn} give 75Fra and 75Mül. The expansion of d_{b} and compression of d_{Li} cause the maximum melting point of the phase.

$\text{Li}_{13}\text{Sn}_5$ (H13.5,SR41.88,drw75Mül.25) replacement-htp Li, four Sn are associated to pairs along a_3 with distance near $\sqrt{3}a_{\text{Li}}/2$, the remaining Sn is single. $a(33,76,40,50)=\text{H}4.70;17.12\text{Å}=b_{\text{FH}}(2;9/3)=g_{\text{CH}}(4;36/3)$. Assuming some more b electrons contributed by Sn, the b correlation may be unstrained.

Li_5Sn_2 (R5.2;SR41.88,drw75Mül.21) replacement-htp Li, all Sn are associated to pairs along a_3 . $a(39,90,48,60)=\text{H}4.74;19.83\text{Å}=b_{\text{FH}}(2;10/3)=g_{\text{CH}}(4;40/3)$. Sn needs no more electrons to be excited into b .

Li_7Sn_3 (M14.6,SR40.86,drw75Mül.15) replacement -htp Li, $a=a_{\text{Li}}(2,1,0.5;2,-1,0.5;0,0,2.5)$, the six Sn per cell form two broken Sn_3 chains. $a(38,88,48,60)=9.45,0,-2.35;4.72;8.23\text{Å}=b_{\text{F}}(2\sqrt{2};\sqrt{2};2.5)=g_{\text{C}}(8\sqrt{2};4\sqrt{2};10)$, $N_{\text{oc}}(g)=0.37$. The remarkable feature that contrary to LiSi_M and LiGe_M no lacunae occur is a consequence of the site number rule (83Sch).

LiSn (M3.3,SR39.82,drw75Mül.77,78) displays straight Sn_∞ chains along a_2 , alternating with straight parallel Li_∞ chains in the quasi hexagonal a_1, a_2 plane. Three such planes are quasi close packed and stacked in the sequence $+ - +$. LiSn is therefore no longer closely htp

CsCl. $a(15,36,24,30)=5.17,0,-1.94;3.18;7.49\text{\AA}=b_{\text{F}}, (1.63;1;2.5)=g_{\text{C}}(6.5;4;10)$, $N_{\text{oc}}(g)=0.4$. The slightly overoccupied b indicates Hund insertion (F) at Sn. The commensurability element 10 in fact favours the observed stacking sequence according to 84Sch.

$\text{Li}_2\text{Sn}_5(\text{Mn}_2\text{Hg}_5, \text{T4.10, SR34.99, drw64Sch.289})$ shows Li_x and Sn_x chains parallel to a_3 . $a(44,108,80,100)=10.72;3.13\text{\AA}=b_{\text{F,U}}(\sqrt{20};2/2)=g_{\text{C}}(\sqrt{160};4)$, $N_{\text{oc}}(g)=0.52$. The low occupancy of g is caused by the high b concentration. The apparent overoccupation of b is caused by Hund insertion.

$\text{Li}_{22}\text{Pb}_5(\text{F88.20, Li}_{22}\text{Tl}_5, \text{SR22.158, phd58Han})$, $a(672,1504,640,1120)=20.08\text{\AA}=b_{\text{FU}}(8;11/2)=g_{\text{C}}(24)$. The under-occupation of 704 b sites needs not be considered prohibitive since the e band may contribute electrons, $N_{\text{oc}}(g)=0.28$.

$\text{Li}_7\text{Pb}_2(\text{H7.2, SR20.137, drw64Sch.225})$, cmp 726°C, is replacement-htp Li. $a(15,34,16,28)=\text{H4.75};8.59\text{\AA}=b_{\text{H}}(2;3.75)=g_{\text{CH}}(4;18/3)$, $N_{\text{oc}}(g)=0.32$. The b correlation is not a sublattice of g and remains therefore somewhat tentative.

" $\text{Li}_{10}\text{Pb}_3(\text{Cu}_9\text{Al}_4, \text{SR7.113})$ " must be replaced by Li_7Pb_2 .

$\text{Li}_3\text{Pb}(\text{Fe}_3\text{Si, Li}_3\text{Pd, h, SR20.136})$, $a(28,64,32,56)=6.69\text{\AA}=b_{\text{F}}(2;3.5/2)=g_{\text{C}}(8)$, $N_{\text{oc}}(g)=0.35$. Here also b is only partially a sublattice of g . It is of interest whether Li_3Pb transforms at low temperatures.

$\text{Li}_8\text{Pb}_3(\text{N8.3, SR20.136, drw64Sch.225})$ is replacement-htp Li. While $\text{Li}_{3.5}\text{Pb}$ has a stacking sequence of layers parallel to the hexagonal basal plane of 3LiPb4LiPb , and Li_3Pb of 3LiPb3LiPb , the phase $\text{Li}_{2.7}\text{Pb}$ has a sequence of 3LiPb2LiPb3LiPb .

$\text{LiPb.h}(\text{CsCl, Li}_{1.1}\text{Au}_{0.9}, \text{SR8.92, 21.145})$ cmp 482°C, $a(5,12,8,14)=3.59\text{\AA}=b_{\text{FU}}(1.5;2.2/2)=g_{\text{B}}(3)$, $N_{\text{oc}}(g)=0.72$. There are many electrons contributed by Pb so that g_{C} is replaced by g_{B} .

$\text{LiPb.r}(\text{R1.1, SR21.145})$, $a(15,36,24,42)=\text{H4.96};6.17\text{\AA}=b_{\text{CH}}(\sqrt{3};6/3)=g_{\text{BH}}(3;18/3)$. The b correlation is in fact a sublattice of g and the compression of b in a_3 direction explains the strain of a in a_3 direction.

$\text{Li}_3\text{P}(\text{Na}_3\text{As, H6.2, SR5.7, drw64Sch.229})$ obeys Lewis' rule and is lacuna htp Li and Li_7Pb_2 because of the high b contribution of P. $a(16,28,4)=\text{H4.27};7.58\text{\AA}=b_{\text{FH}}(2;4.5/3)=g_{\text{BH}}(2;18/3)$, $N_{\text{oc}}(g)=0.61$. With the heavy homologue Bi the Lewis phase $\text{Li}_3\text{Bi}(\text{Fe}_3\text{Si})$ is formed which does not contain lacunae conforming to the site number rule (see 75Mül.100).

$\text{Li}_2\text{P}(\text{J. Am. Ch. Soc. 73.2038})$.

$\text{LiP}(\text{LiAs, M8.8, 71Eck, drw64Sch.242})$ has only one uncompensated spin per anion like $\text{LiCl}(\text{NaCl})$, but it is only loosely htp NaCl because of the spin compensation from P to P. $a(48,80,16)=4.94;4.98;-2.53,0,10.19\text{\AA}=b_{\text{C}}(\sqrt{10};\sqrt{10};6.5)=g_{\text{F}}(\sqrt{10};\sqrt{10};6.5)$, $N_{\text{oc}}(g)=0.49$. The b correlation is strongly overoccupied so that it would be of interest how much Mg might replace Li. The rare g_{F} correlation appears to be intermediate between g_{B} of Li_3P and g_{C} of Li_3As .

$\text{Li}_3\text{P}_7(\text{O, 85Vil})$, $a(\dots)=9.75;10.53;7.60\text{\AA}$. The polyphosphides have complicated structures so that binding proposals can be no more than tentative.

- LiP₅(O4.20,SR38.117,drw ibid.), $a(104,168,40)=10.44;6.58;6.55\text{\AA}=b_{\text{C}}(4;6.5)=g_{\text{C}}(\sqrt{32};9)$.
- LiP₇(U8.56,SR38.117,drw ibid.), $a(576,928,224)=13.42;14.65\text{\AA}=b_{\text{C}}(6;8)=g_{\text{FV}}(12;18/2)$,
 $N_{\text{oc}}(g)=0.67$.
- LiP₁₅(NaP₁₅,77vSch).
- Li₃As(Na₃As, Li₃P, SR23.38), $a(16,32,16,16)=\text{H}4.38;7.80\text{\AA}=b_{\text{FH}}(2;4/3)=g_{\text{CH}}(4;18/3)$,
 $N_{\text{oc}}(g)=0.28$.
- LiAs(M8.8, LiP, SR23.38), $a(48,96,64,64)=5.14;5.24;-2.66,0,10.79\text{\AA}=b_{\text{C}}(\sqrt{10};\sqrt{10};6.5)=g_{\text{C}}(\sqrt{40};\sqrt{40};13)$, $N_{\text{oc}}(g)=0.52$.
- Li₃Sb.h(Na₃As, Li₃P, SR5.7, phd77Mof), $a(16,32,16,20)=\text{H}4.71;8.33\text{\AA}=b_{\text{FH}}(2;4.33)=g_{\text{CH}}(4;17/3)$, $N_{\text{oc}}(g)=0.31$.
- Li₃Sb.r(Fe₃Si, Li₃Pd.h, SR5.60), $a(32,64,32,40)=6.75\text{\AA}=b_{\text{F}}(2)=g_{\text{C}}(8)$, $N_{\text{oc}}(g)=0.33$, the heterotypism h-r obeys the site number rule.
- Li₂Sb(Mg₂Ga, H12.6, SR43.15, drwSR35.63), is a sheared C_H type of Li (stacking sequence + -), $a=a_{\text{CH}}(\sqrt{3};4/3)$, with Sb in the octahedral channels along a_3 , but in triangular coordination. $a(42,84,48,60)=\text{H}7.95;6.53\text{\AA}=b_{\text{FH}}(\sqrt{12};3.5/3)=g_{\text{CH}}(\sqrt{48};14/3)$, $N_{\text{oc}}(g)=0.35$. Since the g lattice in the basal plane is fine, as compared with the Li lattice, the g correlation may be considered as smeared in that plane. For 2 Li layers parallel to a_1, a_2 there are 7 g layers so that the stacking rule (84Sch) is fulfilled. The high number of Li lacunae as compared with a Li_{B1} array will be also found in Li₂O(CaF₂) below. Therefore Mg₂Ga and CaF₂ are homeotypic.
- Li₃Bi(Fe₃Si, Li₃Pd.h, SR3.637, phd58Han) cmp 1145°C. $a(32,64,32,56)=6.72\text{\AA}=b_{\text{F}}(2)=g_{\text{C}}(8)$, $N_{\text{oc}}(g)=0.36$.
- LiBi.h.
- LiBi.r(CuAu, SR3.638), $a(6,12,8,14)=3.37;4.26\text{\AA}=b_{\text{F}}(1;1.25)=g_{\text{C}}(4;5)$, $N_{\text{oc}}(g)=0.5$. Remarkably b takes only 5 electrons. It must be assumed that one b electron is in Hund insertion.
- Li₂O(CaF₂, SR3.283) is a Lewis phase obeying Zintl's rule. $a(8,40)=4.61\text{\AA}=b_{\text{C}}(2)=g_{\text{C}}(4)$, $N_{\text{oc}}(g)=0.75$. The phase is homeodesmic to Li(W), one O causes one lacuna. The high g -occupancy corresponds to the low electron number.
- LiO(H4.4, SR21.233) is a peroxide since spin compensation is partly between O so that O₂ dumbbells (parallel to a_3) are formed. It does not appear desirable to express the peroxoyd property in the chemical formula (Li₂O₂) since other spin structures (for example magnetism) are also not expressed in the formula. $a(4,32)=\text{H}3.14;7.60\text{\AA}=b_{\text{CH}}(1;6/3)=g_{\text{CH}}(2;12/3)$, $N_{\text{oc}}(g)=0.75$. The phase is isodesmic to Li₂O but the number of g sites per atom is 5.3 in Li₂O and 6 in LiO because of the higher b concentration.
- LiO₂.l(O2.4, 75Pie), $a(2,28,8)=5.91;4.94;3.28\text{\AA}=g_{\text{C}}(5;4;2.5)$.
- Li₂S(CaF₂, Li₂O, SR3.20, phd77Mof) cmp, $a(32,48,8)=5.72\text{\AA}=b_{\text{F}}(2)=g_{\text{B}}(4)$, $N_{\text{oc}}(g)=0.69$. It appears that LiS does not exist since the b electrons are less close together than in LiO.
- Li₂Se(CaF₂, Li₂O, SR3.20, phd77Mof) cmp 1302°C, $a(32,56,32,32)=6.02\text{\AA}=b_{\text{F}}(2)=g_{\text{C}}(8)$, $N_{\text{oc}}(g)=0.30$.

$\text{Li}_2\text{Te}(\text{CaF}_2, \text{Li}_2\text{O}, \text{SR}3.20, \text{phd}77\text{Mof})$ cmp 1204°C , $a(32,56,32,40)=6.52\text{\AA}=b_{\text{F}}(2)=g_{\text{C}}(8)$, $N_{\text{oc}}(g)=0.31$.

$\text{LiTe}_3(\text{H}12.36, \text{SR}43.79)$ cmp 460°C , $a(12+216,24+360,288,360)=\text{H}8.71; 21.35\text{\AA}=b_{\text{F}\cdot\text{H}}(4; 12)=g_{\text{CH}}(8; 48/3)$. Hund insertion is 1 electron per Te while it is two in Te(Se).

$\text{LiF}(\text{NaCl}, \text{SR}1.73)$ is a Lewis phase following Zintl's rule, cmp 870°C , $a(32,16)=4.03\text{\AA}=b_{\text{F}}(2)=g_{\text{C}}(4)$, $N_{\text{oc}}(g)=0.75$. The high b contribution of the anion does not admit non-Lewis phases.

$\text{LiCl}(\text{NaCl}, \text{SR}1.73)$, $a(32,40,8)=5.15\text{\AA}=b_{\text{F}}(2)=g_{\text{B}}(4)$, $N_{\text{oc}}(g)=0.63$. LiCl and LiAl have both $a=b_{\text{F}}(2)$, but obeying Bradley's rule the higher b concentration causes a lower atomic concentration in LiCl .

$\text{LiBr}(\text{NaCl}, \text{SR}1.73)$, $a(32,48,32,32)=5.50\text{\AA}=b_{\text{F}}(2)=g_{\text{C}}(8)$, $N_{\text{oc}}(g)=0.28$.

$\text{LiI}(\text{NaCl}, \text{SR}1.73)$, $a(32,48,32,40)=6.01\text{\AA}=b_{\text{F}}(2)=g_{\text{C}}(8)$, $N_{\text{oc}}(g)=0.30$. The very low g occupancy in the two last phases is caused by the high b contribution of the anion. The influence of the f electrons becomes negligible. The end of the bonding contribution is reached in the noble gas elements crystallizing only at very low temperatures.

Discussion

The above binding proposals give simple replies to simple questions which are frequently not answered by earlier models.

Why are in LiA_M^I no intermediate phases? There is no opportunity of expansion of higher filled b shells of the A component or of compression of the large volume of Li by correlative forces.

Why is a Laves phase such as Li_2Ca missing in LiSr_M and LiBa_M ? The electron rule $N_b(\text{Sr})=2N_b(\text{Li})$ is fulfilled but not the volume rule $V(\text{Sr})=2V(\text{Li})$.

Why opens LiSc_M a stability gap? The ratio of distances according to (83Sch) $d_c(\text{Li})/d_c(\text{Sc})=1.8/1.2=1.5$ is far from the harmonic values 1 or 2.

Why does $\text{LiRh}(\text{H}1.1)$ not exhibit a distribution of components like as $\text{AuCd}(\text{O}2.2)$? The hemstitch relation of the g correlations raises the problem of the energy of their fitting surface. It must be of low energy for stability.

Why is LiPd_7 separated from Pd although the g correlation is in both phases the same? The b electrons of Li open a correlation which is exclusively favourable for the composition LiPd_7 .

Why is in LiAg_M no " LiAg_7 " but only $\text{Li}_{\text{in}}\text{Ag}(\text{Cu})$? The b correlation is filled here also by electrons from Ag, therefore LiAg_7 cannot have an outstanding energy.

Why are $\text{LiCd}(\text{NaTl})$ and $\text{LiHg}(\text{CsCl})$ heterotypic? The numbers of g sites per subcell are 64 and 54, the smaller number of g sites per subcell is caused by the higher number of f electrons (rule of site numbers). Therefore the f correlation is responsible for the heterotypism.

Why is Li_5Ga_4 strained in a_3 direction although the b concentration is smaller than in LiGa ? Presumably the larger Li atom causes the effect. For this problem a rule of Frank and Müller (1975) on the bonds between Sn in LiSn_M phases should be considered.

Why occur in LiGe_M lacuna-htps of Li and in LiSn_M not? This is a consequence of the site number rule (83Sch).

Why has LiBi_r only 5 b sites? This may be caused by Hund insertion at Bi.

Why does Li_2S contain lacunae contrary to $\text{Li}_3\text{Bi}(\text{Fe}_3\text{Si})$. This is a case of Bradley's rule conserving the favourable b_f at the expense of atomic density.

Why does the $N_{oc}(g)$ occupancy drop down to 0.28 in LiBr ? The influence of the f electrons becomes so weakened by the high b concentration that it could be neglected. It must be assumed that the f electrons fall out of bonding definitively in the noble gases.

Many answers to various questions should not cause the impression that in the LiA_M phases all is understood now. On the contrary, many new and interesting questions emerge:

Is there a tetragonal low temperature phase of $\text{Li}_{22}\text{Pb}_5$, or is the b correlation twinned at all temperatures?

How are the Ag distributed in Li_9Ag_4 ? Are there really lacunae?

What is the true shear structure of LiAu_ym ?

Which are the structures in the many phases of LiZn_M , LiIn_M etc.?

The easy interpretation of stability in LiA_M phases may stimulate the determination of LiA_M structures which have remained unsolved so far. Each new structure provides an examination of the valence model and will eventually contribute to its improvement.

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