Growth of New Intermetallic Compounds from Aluminum Flux

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Intermetallics

Molten metals as solvents for crystal growth

$RE[AuAl_2]_nAl_2(Au_xSi_{1-x})_2$ series

Discovery of new $REAu_3Al_7$ ternary

$M_3Au_7Al_{26}Ti$ phase from reduction of perovskites

Intermetallic Compounds

Combination of two or more metallic or semimetallic elements -- a range of materials falling between metal alloys and zintl phases.

Electrons are delocalized, but some charge transfer and polarity is present in the compounds. Simple electron counting rules not necessarily applicable.

Ionic: high electronegativity difference, charge localized; valence rules

Metallic--electrons fully delocalized; larger phase width

Salts	Zintl phases	Polar intermetallics	Intermetallics	Metals, alloys
NaCl, $CaTiO_3$	Na_4Si_4, NaTl	$CeAuAl_3$, $BaCu_5Al_8$	$PtAl_2$, $TiAl_3$	Brasses, PbSn

Complex structures, metallic conductivity, magnetism, superconductivity. Additional elements add to complexity, tailorability of products

Traditional solid state synthesis--combine stoichiometric ratios and heat to high temperature

Metal fluxes

Solution phase growth--large crystals (better for structure determination, transport measurements, etc.)

Low temperature--metastable/kinetic phases

Good for exploratory synthesis--allows reactants to find a product with low energy structure

Selection of flux:

- solubility of reactants
- formation of binaries with reactants
- ease of removal from products

Quaternary intermetallics grown in Al flux

Combination of elements from different sections of periodic table

- Rare earths (magnetism)
- Tetrelides (silicon or germanium--temperature resistance)
- Transition metals (magnetism, catalysis)

Studies using 1st and 2nd row transition metals produced many new structures

$Sm_2Ni(Ni_xSi_{1-x})Al_4Si_6$,[1] $RE_4Fe_2Al_7Si_8$,[2] $RE_8Ru_{12}Al_{49}Si_9(Al_xSi_{12-x})$[3]

Investigation of 3rd row transition metals to explore reactivity

- Au, Pt highly electronegative
- Used in electronics, catalysis

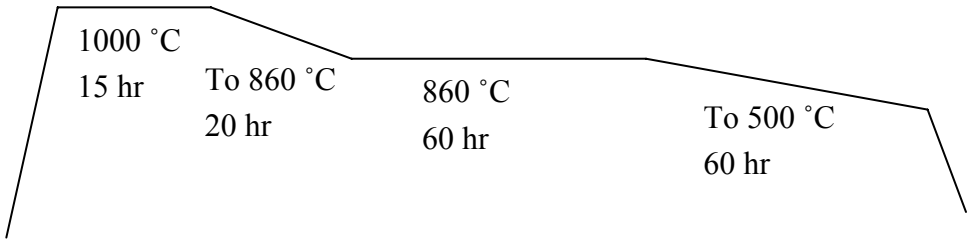
[1]Chen, X.Z. et al. *Chem. Mater*. **1998**, *10*, 3202. [2]Sieve, B. *Chem. Mater*. **2001**, *13*, 273. [3]Sieve, B. *J. Am. Chem. Soc.* **2001**, *123*, 7040.

Synthesis in Aluminum Flux

Rare earth, transition metal, and silicon reacted in aluminum flux

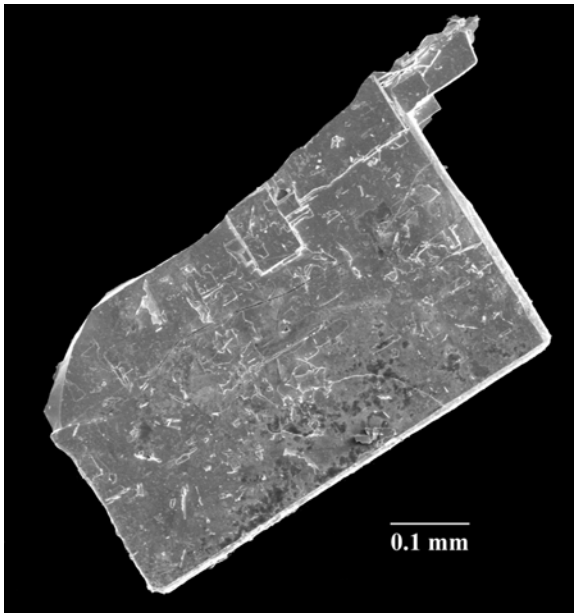
Reactants are placed in an alumina crucible which is then sealed within a quartz tube.

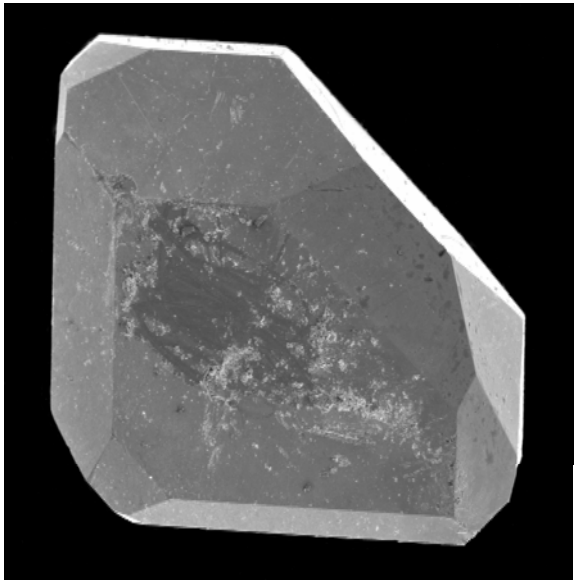
Heating profile



Flux removed with 5M NaOH

Crystals studied by elemental analysis, XRD, magnetic susceptibility, band structure calculations, transport measurements



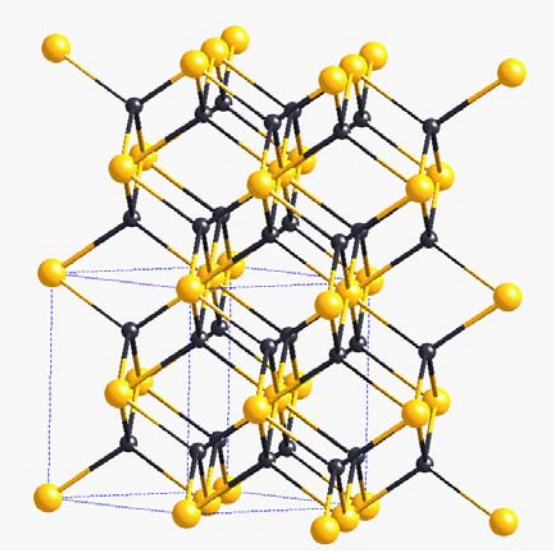


RE/Au/Al/Si: Intergrowths of $AuAl_2$ and $BaAl_4$

All the quaternary structures found in this work feature rare earth ions in $BaAl_4$ type coordination, separated by $AuAl_2$ layers of varying thickness.

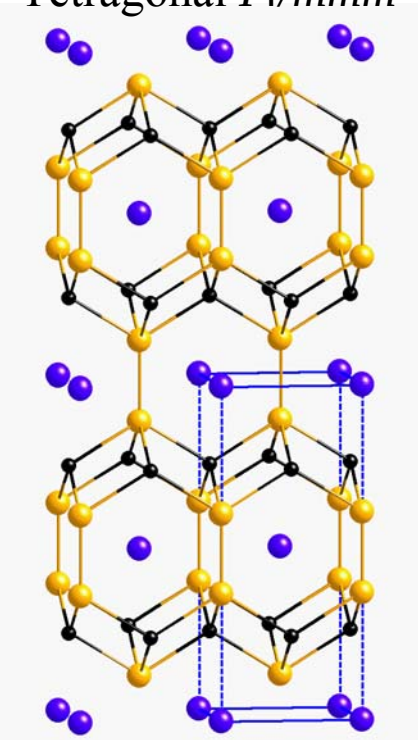
$AuAl_2$: antifluorite structure, tetrahedral Al and Au in cubic environment.

Fm-3*m*, a = 5.997Å.
Au-Al distance 2.597Å



$BaAl_4$: very common structure for binary and ternary intermetallics

Tetragonal *I*4/*mmm*

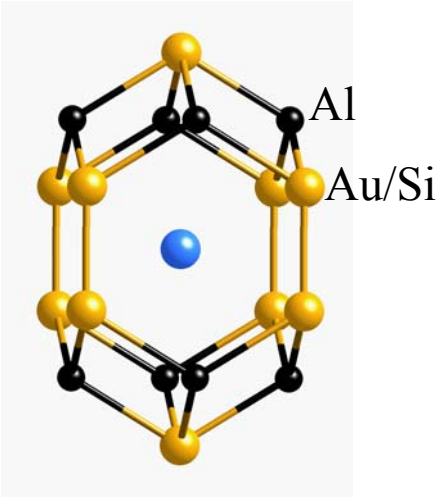


The $RE[AuAl_2]_nAl_2(Au_xSi_{1-x})_2$ series

Intergrowths of $BaAl_4$ layers and slabs of $AuAl_2$ of varying thickness. (n = 0 - 3)

Capping sites of the $AuAl_2$ layers contain a mixture of gold (30-50%) and silicon.

As layers get thicker, bond distances within them become more similar to those found in bulk $AuAl_2$ (Au-Al distance 2.597Å).



$REAuAl_2Si$	$RE[AuAl_2]_0Al_2(Au_xSi_{1-x})_2$	*I4/mmm*	4 x 10 Å
$REAu_2Al_4Si$	$RE[AuAl_2]_1Al_2(Au_xSi_{1-x})_2$	*P4/mmm*	4 x 8 Å
$EuAu_3Al_6Si$	$RE[AuAl_2]_2Al_2(Au_xSi_{1-x})_2$	*I4/mmm*	4 x 22 Å
$REAu_4Al_8Si$	$RE[AuAl_2]_3Al_2(Au_xSi_{1-x})_2$	*P4/mmm*	4 x 14 Å

Possible next homologue:

$REAu_5Al_{10}Si$	$RE[AuAl_2]_4Al_2(Au_xSi_{1-x})_2$	*I4/mmm*	4 x 34 Å

$BaAl_4$ structure: $REAu_{1-x}Al_2Tt_{1+x}$

Tetragonal *I4/mmm*

$LaAu_{0.5}Al_2Si_{1.5}$

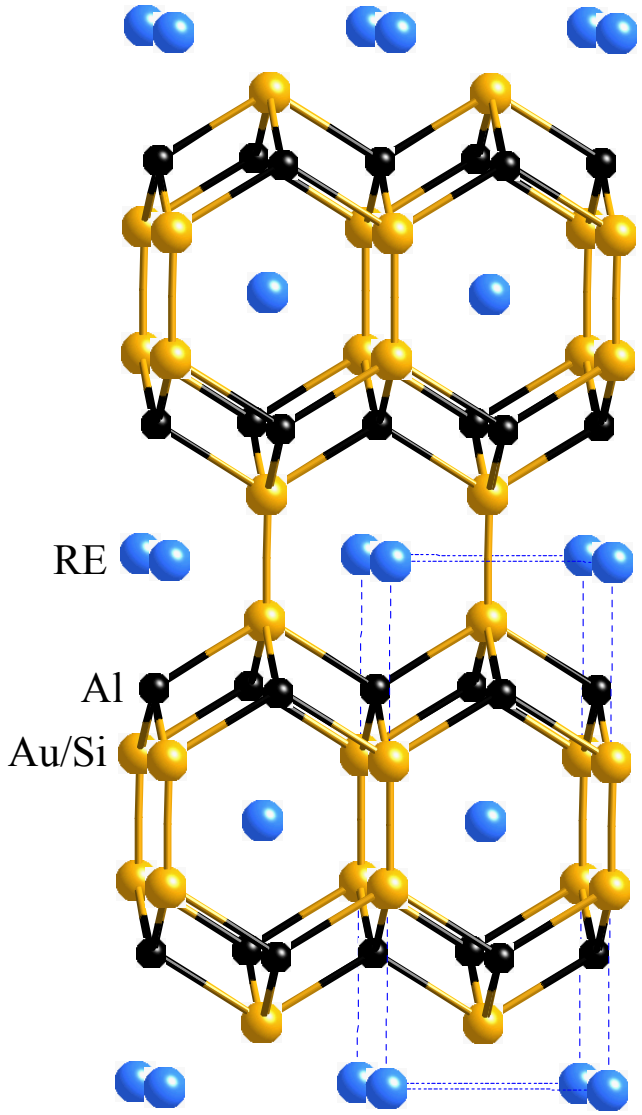
$CeAuAl_2Si$

$NdAuAl_2Si$

Au/Si mixed occupancy site (30-50% Au)

Au/Si - Al distance 2.50-2.55Å

Au/Si - Au/Si distance 2.40-2.50Å

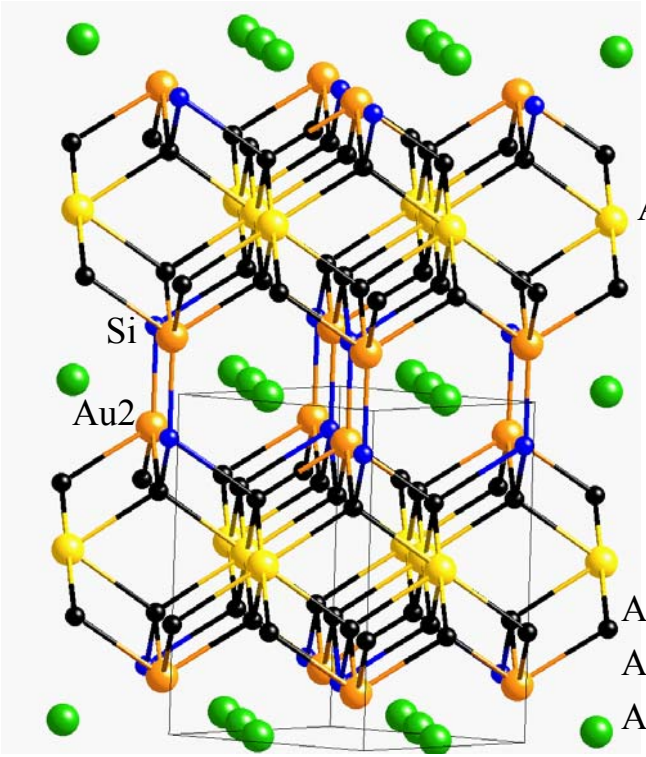


$REAu_2Al_4Si$

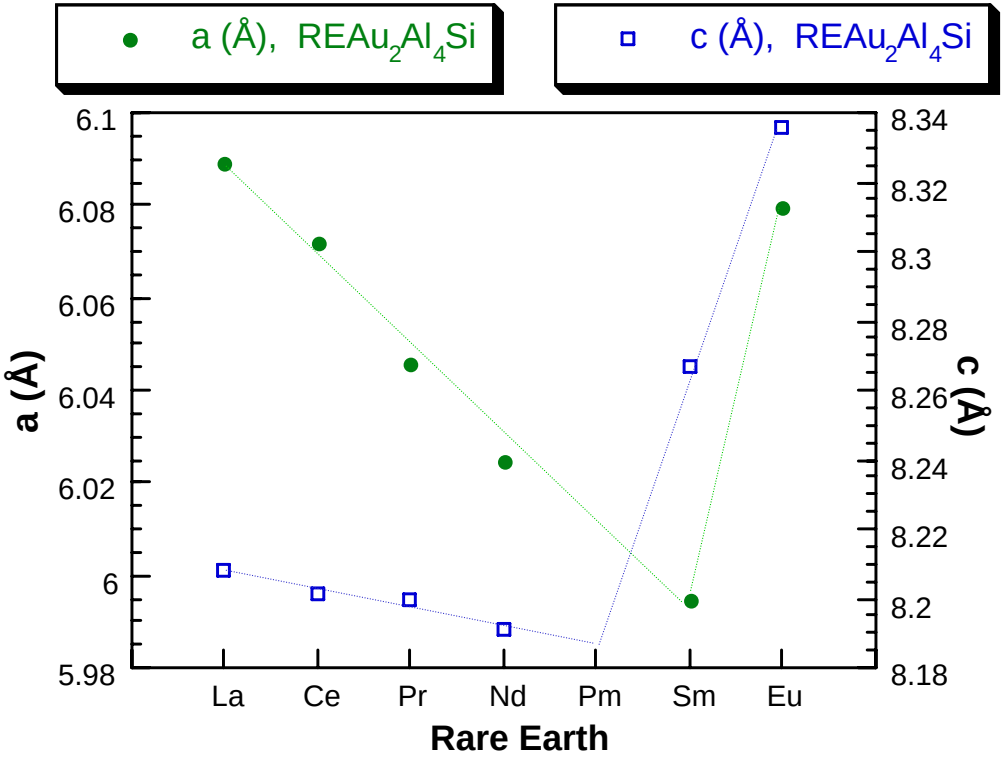
New supercell of the KCu_4S_3 structure

Ordering of Au and Si in the capping sites of the $AuAl_2$ slab lowers the symmetry from *P4/mmm* (KCu_4S_3 type, a ≈ 4Å, c ≈ 8Å) to *P4/nmm* (a* = √2a, c* ≈ 8Å)

Deviation from cell parameter trend indicates Eu analog divalent; confirmed by magnetic susceptibility measurements.



Au1-Al: 2.589Å
Au2-Al: 2.576Å
Au2-Si: 2.442Å



$EuAu_{3-x}Al_6Si_{1+x}$

New tetragonal structure in *I4/mmm*

a = 4.2733(7)Å; c = 22.582(5)Å

This structure only found for RE = Eu thus far.

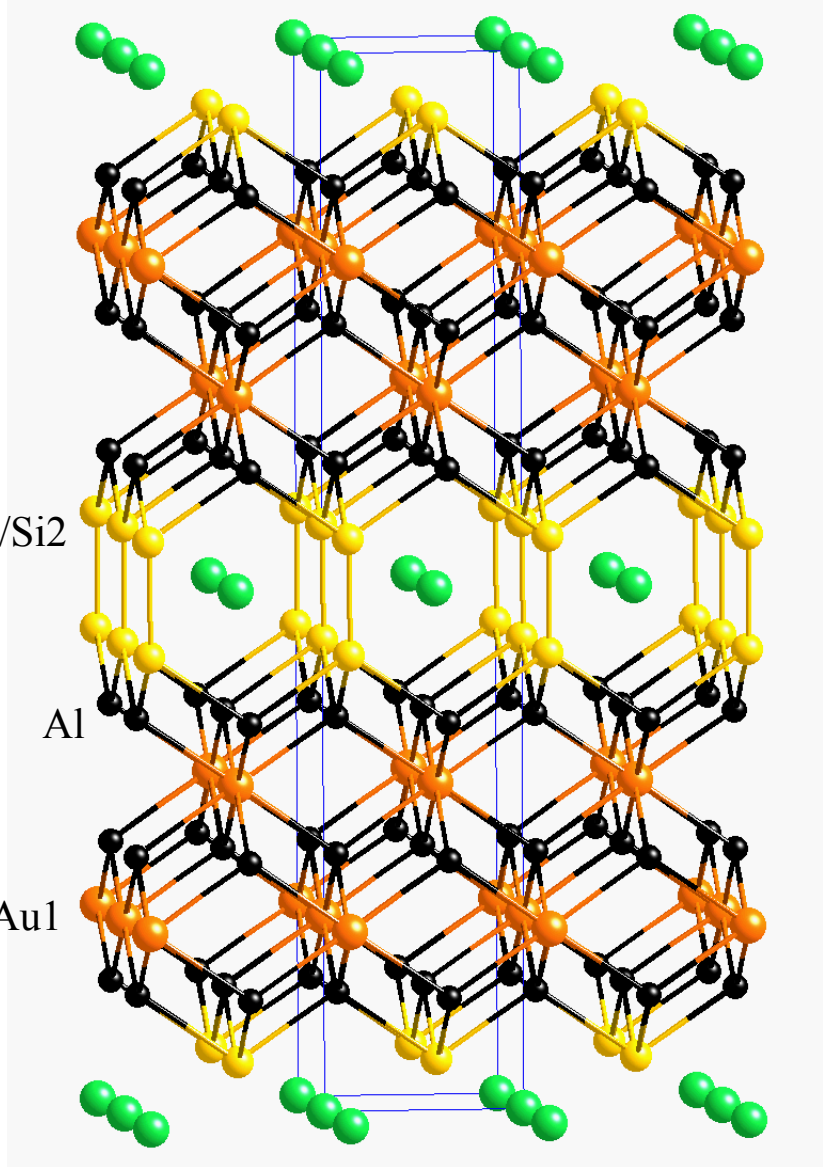
Divalent state of Eu ion confirmed by magnetic susceptibility measurements.

Mixed occupancy site Au/Si2 is 29% Au, 71% Si

Au1-Al: 2.587Å, 2.604Å

Au/Si2 - Al: 2.587Å

Au/Si2 - Au/Si2: 2.478Å



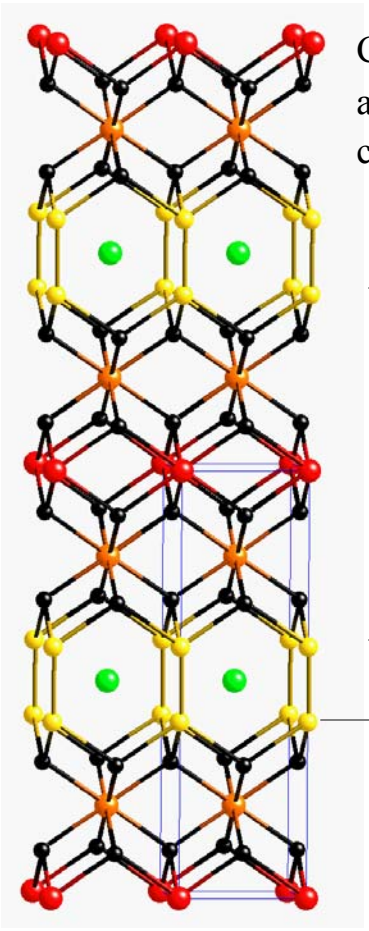
$REAu_{4-x}Al_8Si_{1+x}$

New tetragonal structure in *P4/mmm* found with RE=Ce, Pr, Nd, Sm, Eu, Yb

Superstructure with ordering of Au/Si mixed site found for Sm and Gd. Silicon and gold order in the capping sites, resulting in a *I4/mmm* supercell with $a^* = \sqrt{2}a$; $c^* = 2c$

Disordered $REAu_{4-x}Al_8Si_{1+x}$

P4/mmm, 4 x 14.3Å



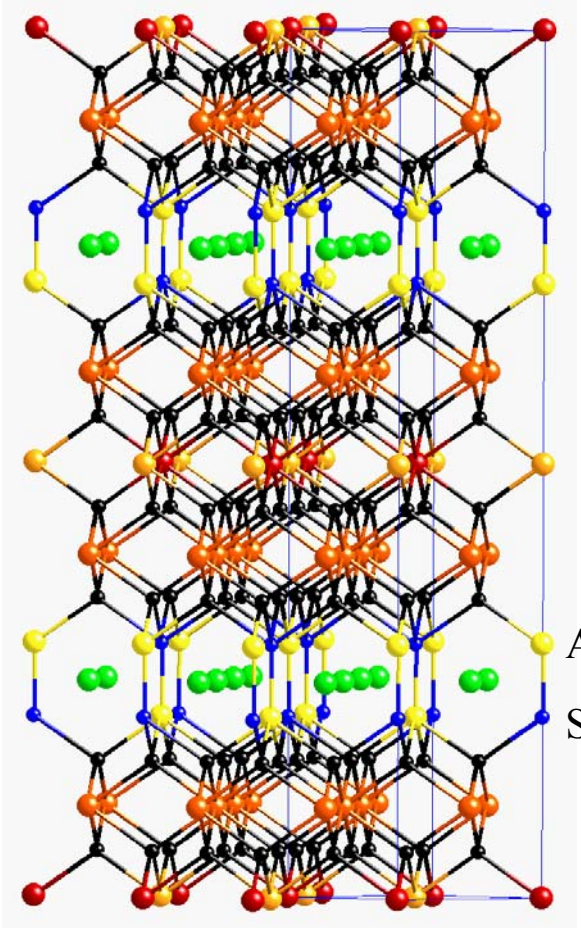
Ce analogue:
a = 4.2577(8)Å
c = 14.211(4)Å

$AuAl_2$ layer
12Å thick

Mixed site:
45% Au / 55% Si

Ordered $REAu_4Al_8Si$

I4/mmm, 6 x 28.6Å



Gd analogue:
a = 5.9788(7)Å
c = 28.627(5)Å

Au

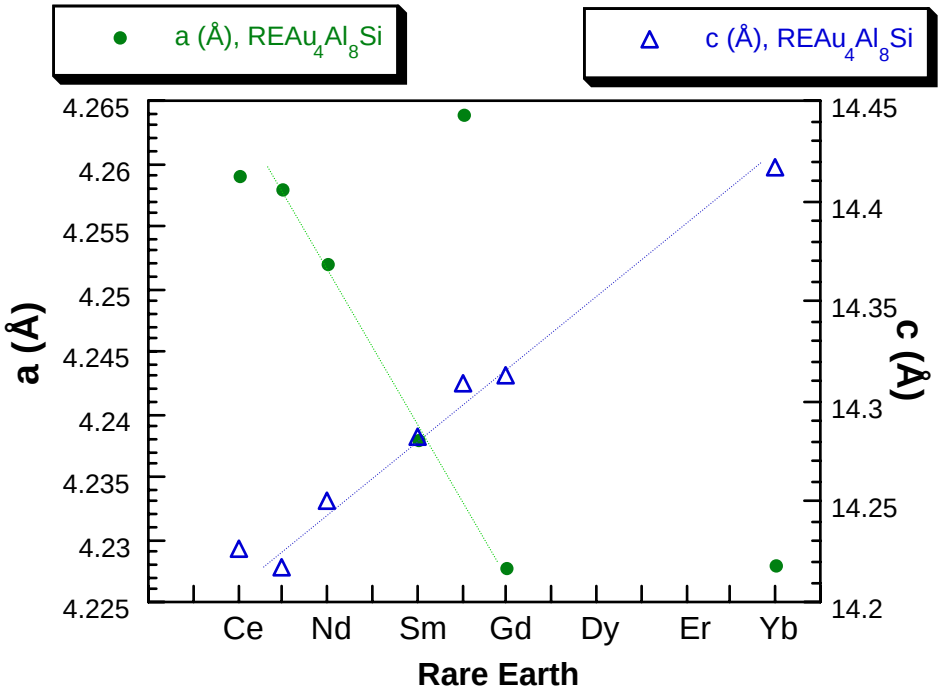
Si

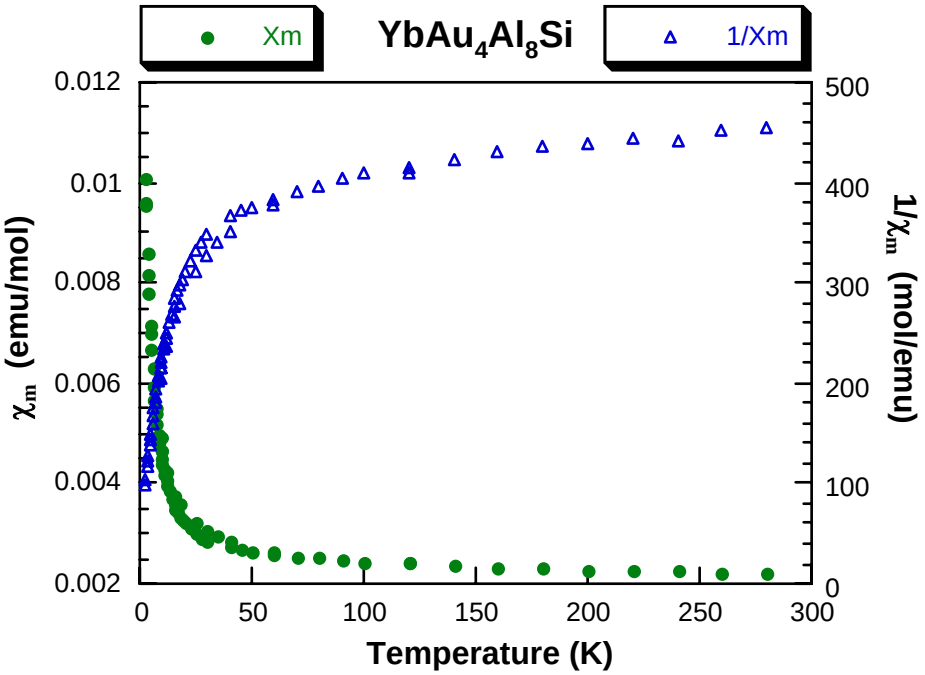
$REAu_4Al_8Si$ Cell Parameters vs RE

The *a* cell parameter decreases as the rare earth radius shrinks; *c* axis elongates but overall cell volume decreases

Ytterbium analogue synthesized, despite lack of other late RE analogues--indicates possible divalence

Unit cell trend anomalies at Ce, Eu, Yb; magnetic susceptibility data indicates divalent europium in $EuAu_4Al_8Si$ and mixed valent Yb^{2+}/Yb^{3+} in $YbAu_4Al_8Si$; Ce results inconclusive

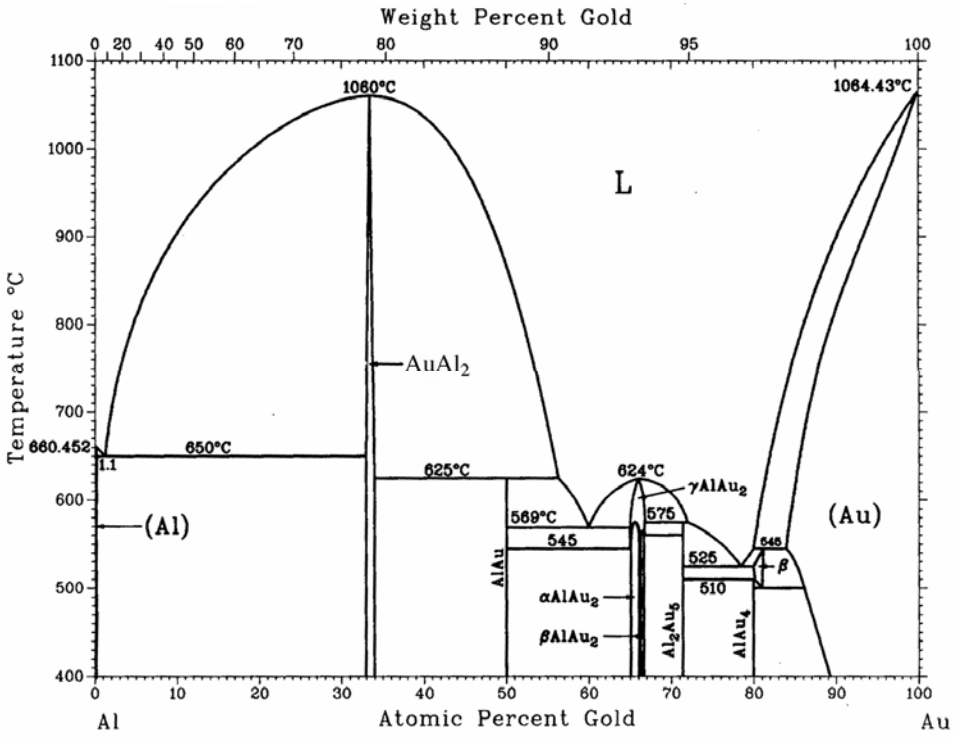




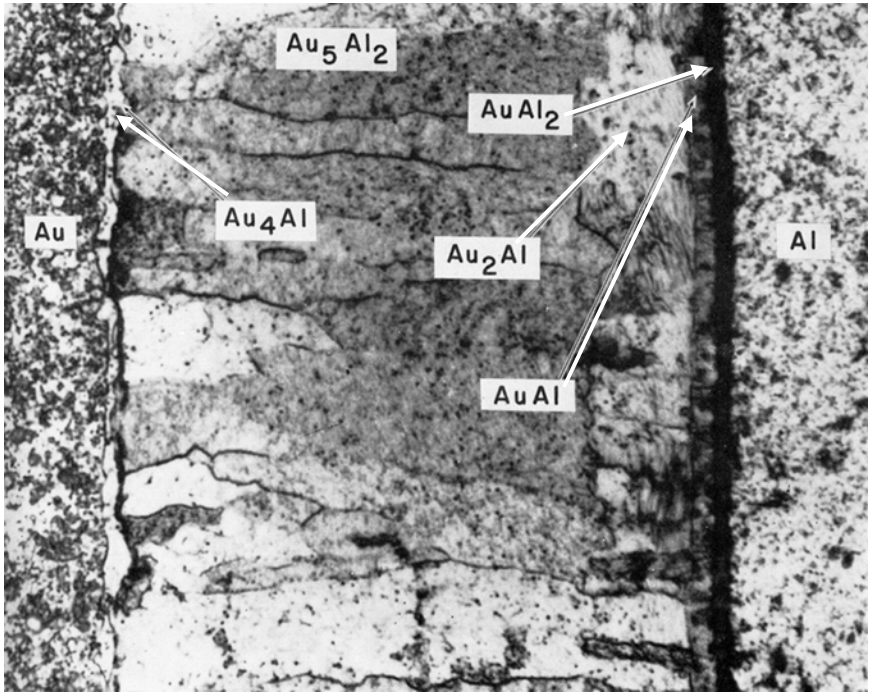
Intermetallic formation in Au-Al contacts

Au-Al contacts are important in the semiconductor industry; studies indicate a series of Au/Al binary intermetallics form at contact points between gold wire and aluminum film.

$AuAl_2$ degrades the wire-film contact due to poor mechanical properties (sometimes referred to as "purple plague" due to its violet color).



Binary Alloy Phase Diagrams, 2nd Ed.
ASM Int.ernational, 1990.

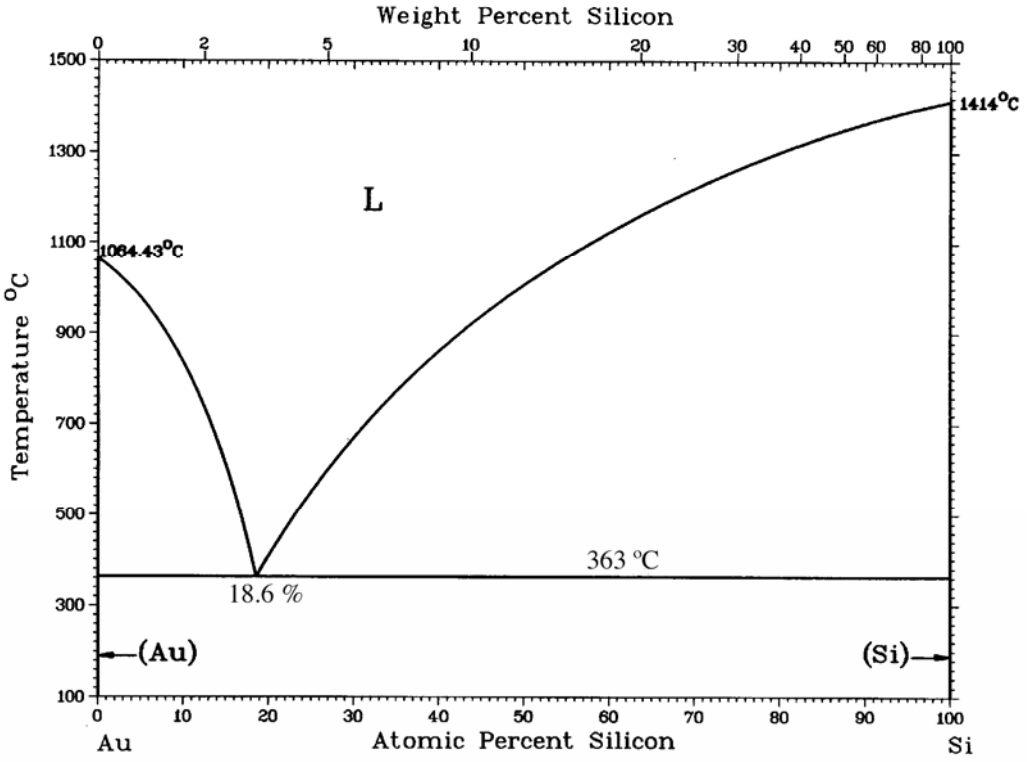


Philofsky, E. *Solid State Elec*. **1970**, *13*, 1638.

Possible effect of silicon on Au-Al interaction

In studies of Au-Al contacts, the presence of Si was found to promote the formation of $AuAl_2$ in the contact region at the expense of the other binary intermetallics.

Constant $AuAl_2$ structural motif in flux-grown RE/Au/Al/Si intermetallics may indicate that a similar process is at work.



Binary Alloy Phase Diagrams, 2nd Ed.
ASM International, 1990.

The ternary Au-Al-Si phase diagram not well-studied.

Extreme eutectic in the Au-Si phase diagram indicates strong interaction of these elements in the liquid state.

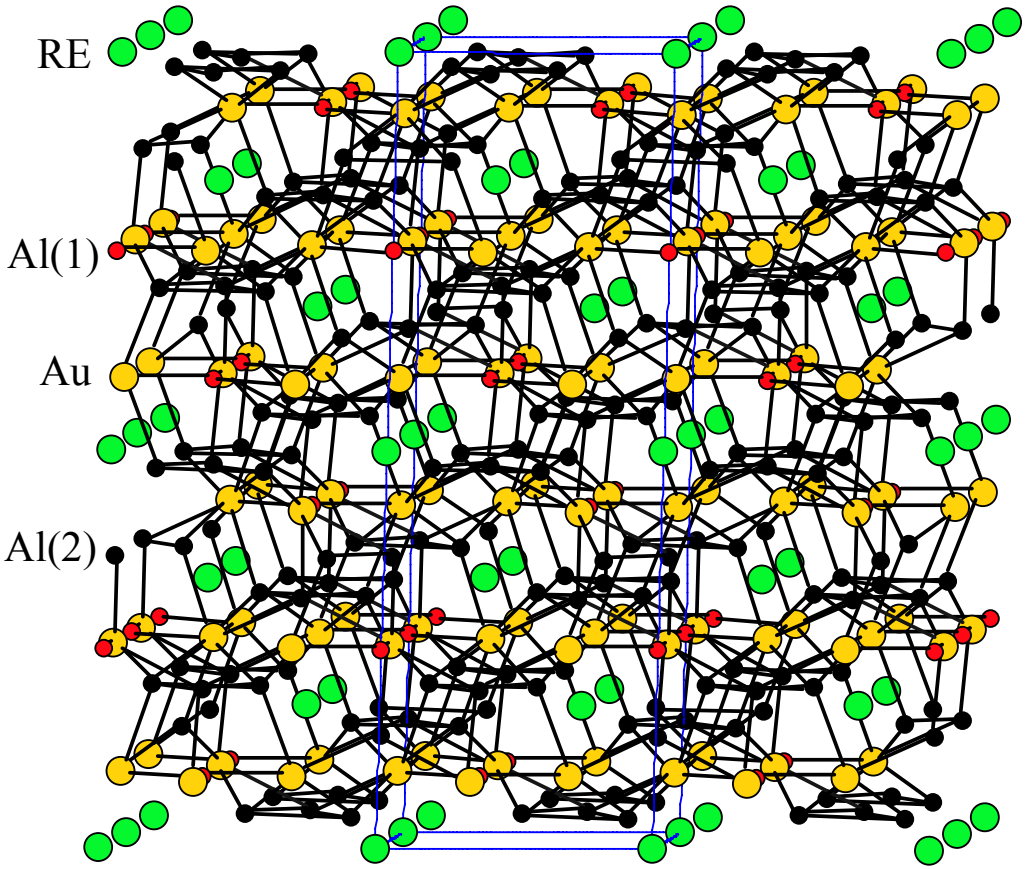
Without Si: new RE/Au/Al ternary phase discovered

Known ternaries: $REAuAl_3$, $REAu_2Al_2$ ($BaAl_4$ type); $La_3Au_2Al_9$ (La_3Al_{11} type)

$REAu_3Al_7$: new phase from flux with complex structure and stoichiometry

Points out usefulness of flux growth for exploratory synthesis

No $AuAl_2$ blocks--Si may be crucial in their formation



$YbAu_3Al_7$

R-3c

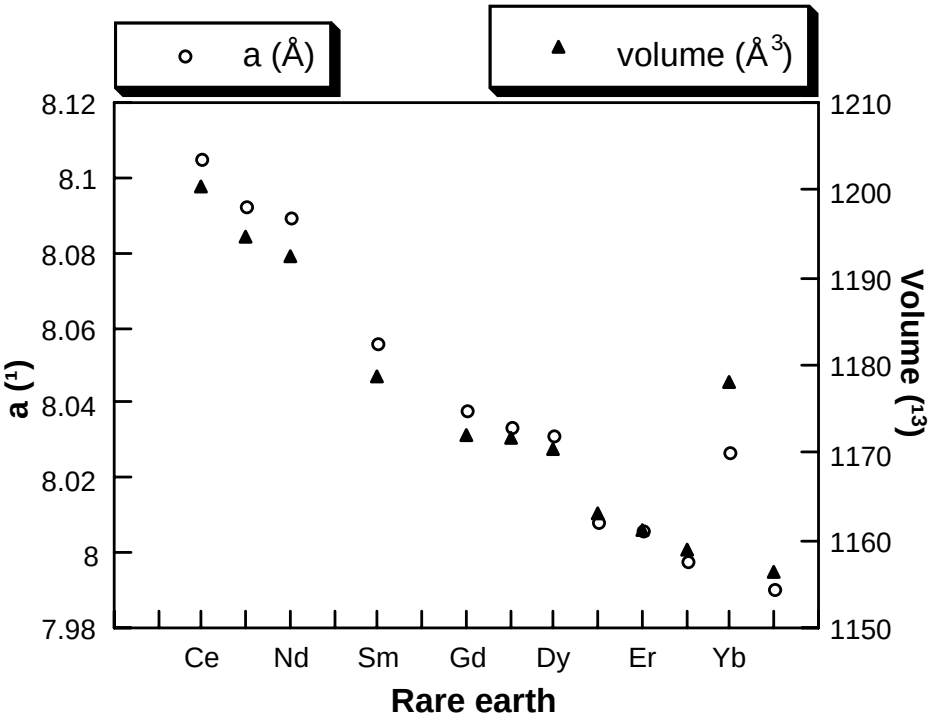
a = 8.0272(9)[1] ; c = 21.111(4)[1]

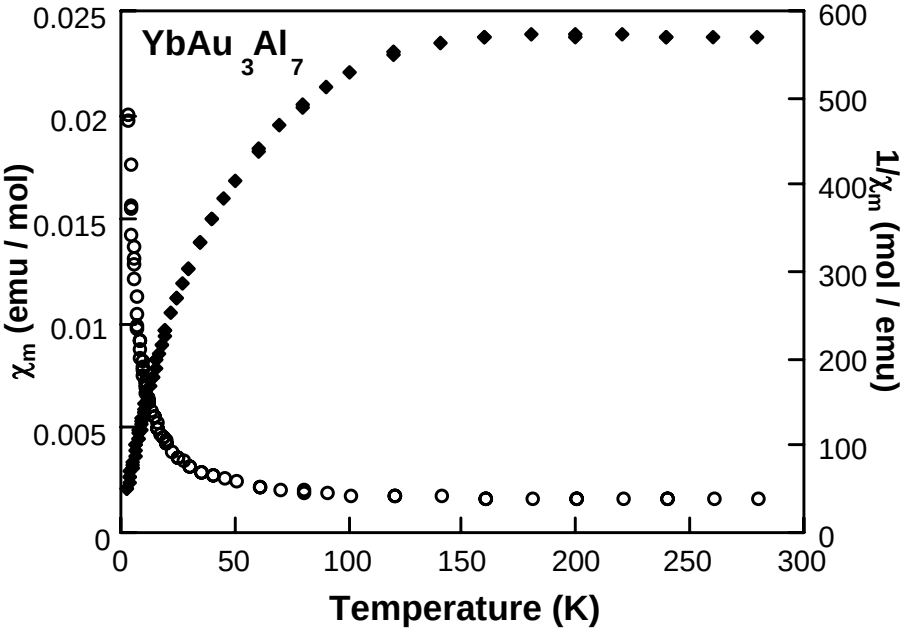
Properties of $REAu_3Al_7$

Forms with all RE except La, Eu--size effects likely

Unit cell parameters decrease regularly across RE, except for Yb

Mixed valence confirmed by magnetic susceptibility, band structure calculations





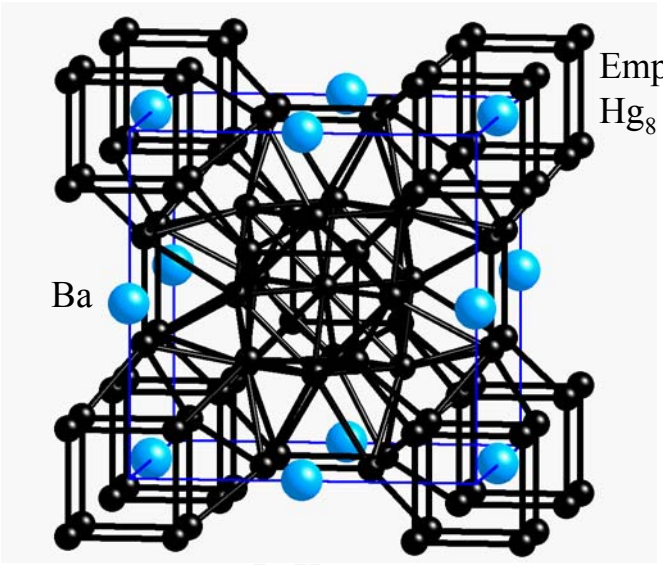
Reaction with early transition metals: $M_3Au_7Al_{26}T$

When silicon in the flux is replaced by an early transition metal T, a modification of the $BaHg_{11}$ structure results--$M_3Au_{6+x}Al_{26}T$

Serendipitous discovery--TiO_2 cement in crucible reacted with Yb/Au/Al reaction mixture

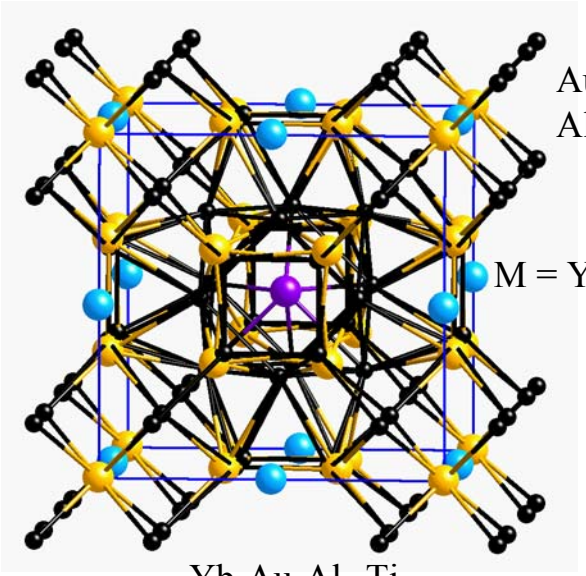
Other known quaternaries of this phase: $Ce_3Cu_7Al_{26}Mn$ as an impurity in an aluminum alloy[1] and $Y_3Ni_7Al_{26}Ta$ as a byproduct of Y/Ni/Al reaction in a Ta container.[2]

Gold analogues form only with divalent or mixed valent M ions: Ca, Sr, Eu, Yb.



$BaHg_{11}$

Pm-3m, a = 9.60[1]



$Yb_3Au_7Al_{26}Ti$

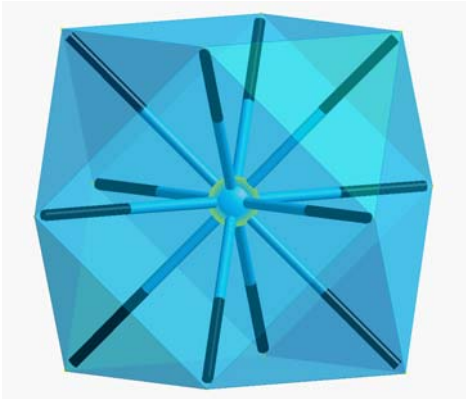
Pm-3m, a = 8.6509(6)[1]

[1]Zarechnyuk, et al. *Inorg. Mater*. **1967**, *3*, 153. [2]Gladyshevskii, et al. *J. Alloys and Cmpds*. **1996**, *240*, 266.

Incorporation of a wide range of transition metals

$M_3Au_7Al_{26}T$ forms with T = early transition metal from groups 4-7; does not form with group 3 or group 8 elements.

Structure type may be templated by the formation of a cuboctahedron of 12 Al around the transition metal.



Compound	Cell (Å)	Compound	Cell (Å)	Compound	Cell (Å)
$Yb_3Au_7Al_{26}Ti$	8.6509(6)	$Sr_3Au_7Al_{26}Ti$	8.7367(6)	$Eu_3Au_7Al_{26}Ti$	8.7094(5)
$Yb_3Au_7Al_{26}V$	8.615(1)	$Sr_3Au_7Al_{26}Cr$	8.692(1)	$Eu_3Au_7Al_{26}V$	8.669(4)
$Yb_3Au_7Al_{26}Cr$	8.5637(9)	$Sr_3Au_7Al_{26}Mn$	8.6851(7)	$Eu_3Au_7Al_{26}Cr$	8.6433(5)
$Yb_3Au_7Al_{26}Mn$	8.552(1)	$Sr_3Au_7Al_{26}Nb$	8.730(3)	$Eu_3Au_7Al_{26}Zr$	8.727(3)
$Yb_3Au_7Al_{26}Zr$	8.6903(5)				
$Yb_3Au_7Al_{26}Nb$	8.653(1)				
$Yb_3Au_7Al_{26}Mo$	8.579(4)	$Ca_3Au_7Al_{26}V$	8.642(2)		
$Yb_3Au_7Al_{26}Hf$	8.6834(8)	$Ca_3Au_7Al_{26}Cr$	8.581(2)		
$Yb_3Au_7Al_{26}Ta$	8.634(2)				

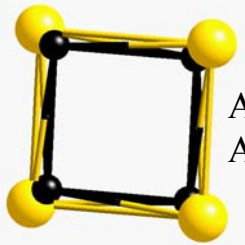
Au/Al split site

Close to 50% occupation of both sites; true structural motif is likely a Au_2Al_2 rhombus

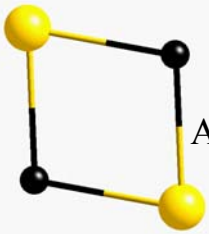
Optimizes Au-Al bond length, Au and Al distance to M ion

Disorder in orientation of rhombi averaged in X-ray data

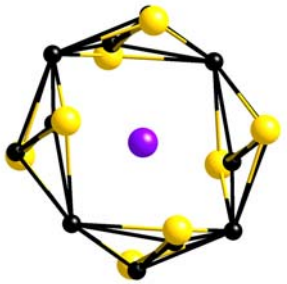
Ordering of rhombi produces a number of possible supercells; *Fm-3m* cell shown below.



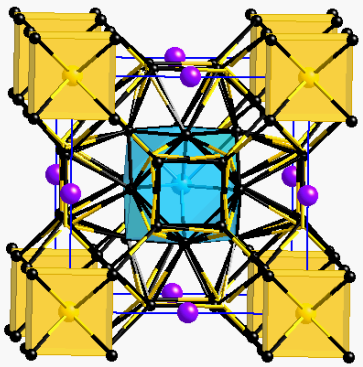
Au-Au: 2.82[1]
Al-Al: 2.33[1]



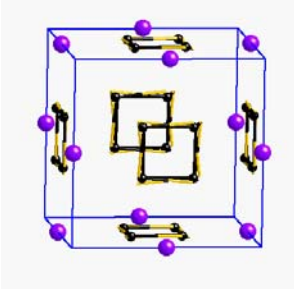
Au-Al: 2.58[1]



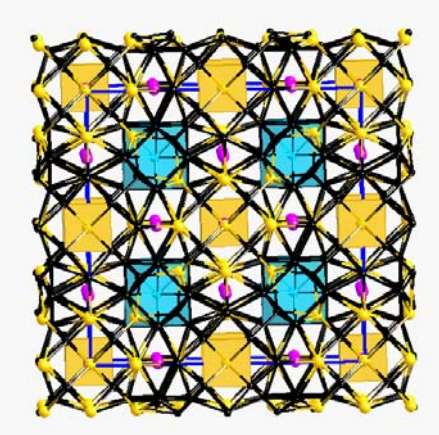
Yb-Au: 3.22[1]
Yb-Al: 3.35[1]



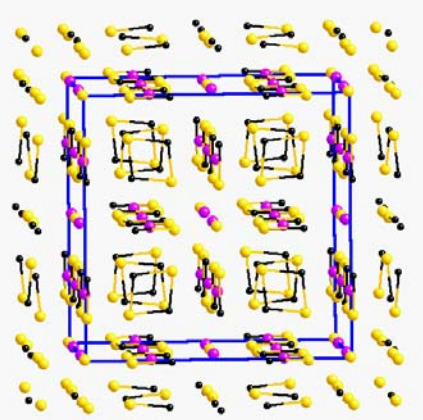
Pm-3m, a=8.7[1]: averaged disordered subcell



The disordered Au/Al split sites



Fm-3m, a = 17.3[1] ordered supercell. Possibly seen in $Ca_3Au_7Al_{26}Ti$.



Ordering of the Au/Al rhombi to form this cell

Reduction of perovskites to form $M_3Au_7Al_{26}Ti$

Al flux attacked TiO_2 in crucible cement to form $Yb_3Au_7Al_{26}Ti$

Reducing power of molten aluminum attacks perovskites

$SrTiO_3$ + Au in Al flux: $Sr_3Au_7Al_{26}Ti$, *Pm-3m*, a = 8.7367(6)[1]

$CaTiO_3$ + Au in Al flux: $Ca_3Au_7Al_{26}Ti$, *Fm-3m*, a = 17.216(2)[1]

$BaTiO_3$ + Au in Al flux: $Ba_3Au_7Al_{26}Ti$, structure in progress

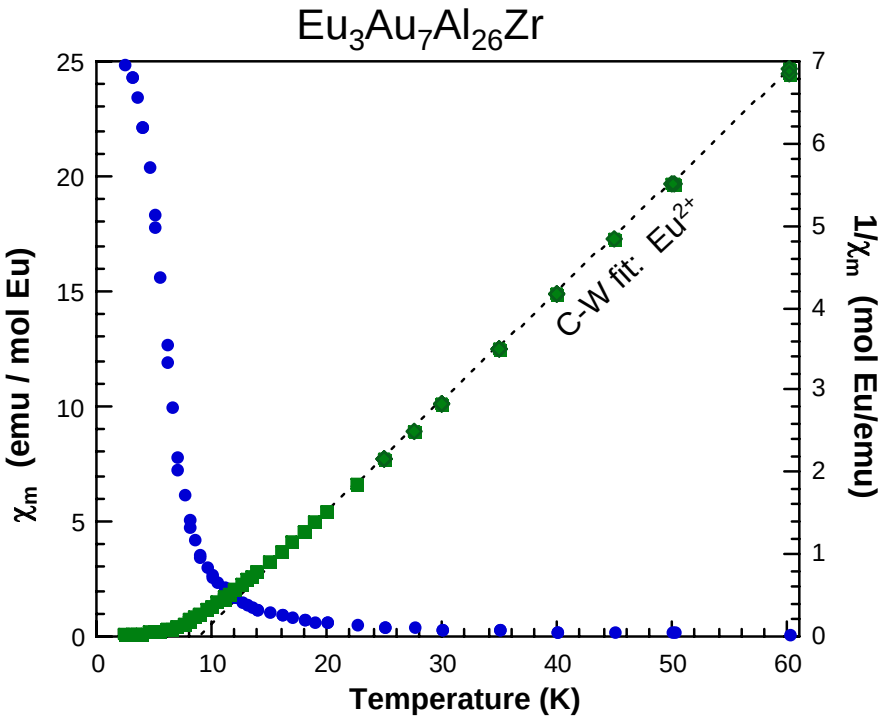
Indicates a wealth of new reactants to explore--multinary oxides

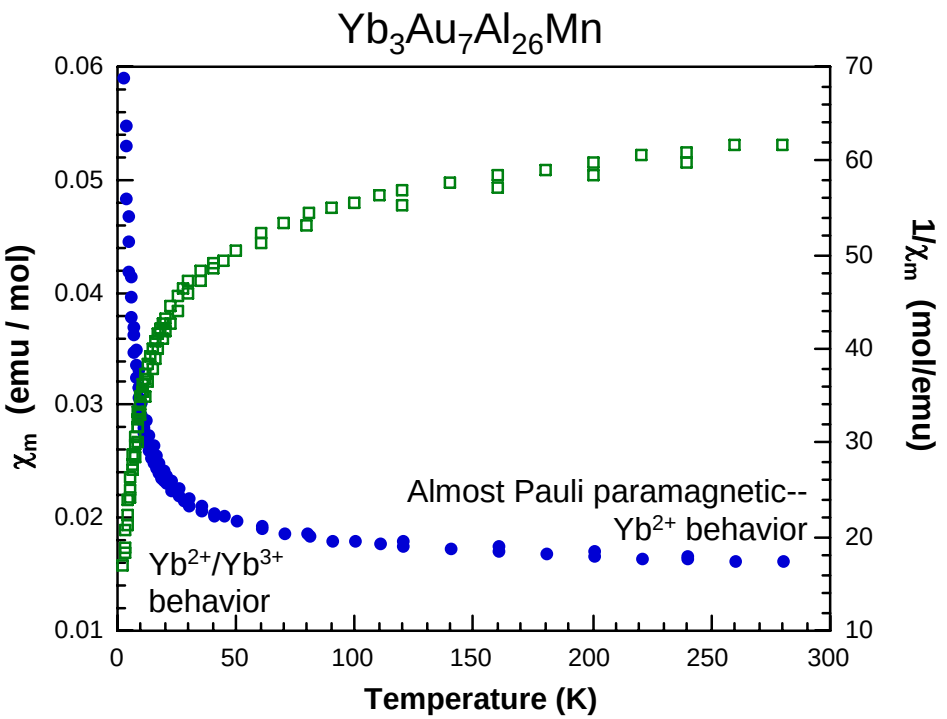
Magnetic susceptibility of $M_3Au_7Al_{26}T$

Initial results indicate the early transition metal T does not play a strong role in the magnetic behavior of the materials. Ca and Sr analogs are Pauli paramagnetic.

Eu analogs: Eu is divalent; ferromagnetic ordering observed at around 10K for $Eu_3Au_7Al_{26}T$ (for T = Ti, Cr, Zr)

Yb analogs: Yb is mixed valent (+2/+3) at low temperatures; $Yb_3Au_7Al_{26}T$ inverse susceptibility does not follow Curie-Weiss behavior for T = Ti, V, Mn, Ta.





Conclusions and future work

- Aluminum flux: an excellent solvent for a wide variety of elements.
- $RE[AuAl_2]_nAl_2(Au_xSi_{1-x})_2$ series and $Th_2(Au_xSi_{1-x})[AuAl_2]_nSi_2$ series: both have $AuAl_2$ slabs of varying thickness, with a mixture of gold and silicon on capping sites.
- Silicon in the reaction mixture seems to play a pivotal role in the formation of $AuAl_2$ slabs within these intermetallics; ternary RE/Au/Al compounds (known and new $REAu_3Al_7$) do not possess similar structural moieties.
- When silicon is replaced by an early transition metal T, a cubic stuffed-$BaHg_{11}$ type structure results. Formation of $R_3Au_7Al_{26}T$ (with R = Yb, Eu, Ca and Sr) may be templated by the favorable cuboctahedral arrangement of 12 Al atoms around the transition metal.

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