Structural Aspects of Chemical Bonding in RTX Intermetallic Compounds*

Andrzej Szytuła

Institute of Physics, Jagiellonian University, 30-059 Kraków, Reymonta 4, Poland
(E-mail: szytula@if.uj.edu.pl)

Unit cell dimensions of ternary RTX intermetallic compounds (R = rare earth metal, T = »nd« transition metal and X = Si, Ge or Sn) are analyzed with respect to the atomic radius of the rare earth component. On the basis of the crystal structure data, information is given on the chemical bonding in these phases.

Key words: crystal structure, chemical bonding, rare earth intermetallic compounds.

INTRODUCTION

Renewed interest has been devoted to the study of the crystallographic and physical properties of the ternary intermetallic compounds RTX with R = rare earth metals, T = nd transition metals and X = Si, Ge or Sn. For the time being, more than 1000 intermetallic RTX compounds are known.[1] They crystallize in more than 30 different crystal structures.[2] Detailed structural analysis of 100 ternary rare earth equiatomic intermetallic compounds RTX with X = Si and Ge was carried out by Hovestreydt *et al*.[3]

A new detailed review of the crystal structure, magnetic and electrical properties of RTX compounds was published by Szytuła and Leciejewicz.[4] The data collected in this book indicate that the crystal structure and physical parameters depend on the composition.

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* Dedicated to Professor Boris Kamenar on the occasion of his 70th birthday.

In this work, the crystal structure of RTX compounds, where T = Cu, Ag, Au and X = Si, Ge or Sn, is discussed. On the basis of the crystal structure data, the chemical bonding in these compounds is analyzed.

CRYSTAL STRUCTURE

Crystal structure data of RTX compounds are reviewed in the paper.[5] Figure 1 collects different structural types presented in the discussed RTX compounds, where T = Cu, Ag, Au and X = Si, Ge, Sn. The majority of these compounds crystallize in hexagonal structures derived from the hexagonal AlB_2-type structure.

X = Si

T \ R	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Cu	x	x	x	x	x		x	x	x	x	x	x	x	x
Ag	▼	▼	▼	▼	●	▼	●	●	●	●	●	●	●	●
Au														▽

X = Ge

T \ R	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Cu	▼	▼	▼	▼	▼	▼	▼	▽	▽	▽	▽	▽	▽	▽
Ag	▽	▽			●	*	●	●	●	●	●	●	●	●
Au	▽	▽	▽	▽	▽	[*]	▽	▽	▽	▽	▽	▽	+	▽

X = Sn

T \ R	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Cu	▽	▽	▽	▽	▽	*	▽	▽	▽	▽	▽	▽	o	▽
Ag	▽	▽	▽	▽	▽	*	▽	▽	▽	▽	▽	▽	□	
Au	▽	▽	▽	▽		*	▽	▽	▽/▲	▽/▲	▲	▲	o	▲

● ZrNiAl	* $CeCu_2$	x ZrBeSi
▼ AlB_2	▽ LiGaGe	▲ MgAgAs
□ CaLiSn	+ CaCuGe	o TiNiSi
[*] ordered version of $CeCu_2$		

Figure 1. Existence and distribution of different structural types in RTX compounds.

Silicides

Among silicides, the RCuSi (R = La...Nd, Sm, Gd...Lu) compounds crystallize in the ZrBeSi-type structure (space group $P6_3/mmc$, No. 194)].[6] The atoms are positioned at the following sites:

2 R atoms in 2(a):   0, 0, 0;   0, 0, ½;

2 T atoms in 2(c):   ⅓, ⅔, ¼;   ⅔, ⅓, ¾;

2 Si atoms in 2(d):   ⅔, ⅓, ¼;   ⅓, ⅔, ¾.

There are no stoichiometric RAgSi compounds with light rare earths. There are RAg_xSi_{2-x} (R = La, Ce, Pr, Nd) compounds that crystallize in the hexagonal AlB_2-type structure (space group $P6/mmm$ No. 191). The atoms are situated as follows:

R atom in 1(a):   0, 0, 0;

Ag and Si atoms (at random) in 2(d):   ⅓, ⅔, ½;   ⅔, ⅓, ½.[7]

The RAgSi (R = Sm...Lu) compounds crystallize in another type of crystal structure.[7,8] It is the hexagonal ZrNiAl-type structure (space group $P\bar{6}2m$, No. 187) with the following distribution of the atoms:

3 R atoms in 3(f): x, 0, 0;   0, x, 0; $\bar{x}$, $\bar{x}$, 0;

3 Ag atoms in 3(g): x, 0, ½;   0, x, ½; $\bar{x}$, $\bar{x}$, ½;

2 Si atoms in 2(d):   ⅔, ⅓, ½;   ⅓, ⅔, ½;

2 Si atoms in 1(a):   0, 0, 0.

In the Eu-Ag-Si system, only $EuAg_{0.67}Si_{1.33}$ composition exists. It crystallizes in the AlB_2-type structure.[9]

The experimental data collected so far show that only compounds with R = Y, Sc and Lu exist in RAuSi system and that they have a hexagonal crystal structure.

The single crystal X-ray data of YAuSi lead to the hexagonal LiGaGe-type structure (also called NdPtSb) (space group $P6_3mc$, No. 186) with the following positions of the atoms:

Y atoms in 2(a):   0, 0, 0;   0, 0, ½;

Au atoms in 2(b):   ⅓, ⅔, 0.234;   ⅔, ⅓, 0.734;

Si atoms in 2(b):   ⅓, ⅔, 0.775;   ⅔, ⅓, 0.275.

The crystal structure of ScAuSi and LuAuSi is described in the space group $P\bar{6}m2$ (No. 187) with the atoms located at:

R atom in 1(a):   0, 0, 0;

R atom in 1(b):   0, 0, ½;

Au atoms in 2(i):   ⅔, ⅓, z_1;   ⅔, ⅓, $\bar{z}_1$;

Si atoms in 2(h):   ⅓, ⅔, z_2;   ⅓, ⅔, $\bar{z}_2$;

where z_1 = 0.258(2) and z_2 = 0.297(2) for ScAuSi and z_1 = 0.2220(5) and z_2 = 0.295(4) for LuAuSi.[10]

Germanides

The X-ray data indicate that the RCuGe compounds containing R = La…Gd, except for Eu, have the AlB_2-type of structure while those containing R = Tb…Lu show the disordered $CaIn_2$-structure type. In contrast, EuCuGe has an orthorhombic structure, similar to that of CaCuGe.[11]

The neutron diffraction data indicate that the RCuGe (R = Tb…Er) crystallize in the ordered LiGaGe-type structure.[12]

The RAgGe compounds exist for R = Y, La, Ce, Sm, Eu, Gd…Lu and, except for R = La, Ce and Eu, they have the ZrNiAl-type hexagonal structure, similar to the one observed in RAgSi.[13,14]

LaAgGe and CeAgGe were found to crystallize in the ordered $CaIn_2$-type structure.[15]

EuAgGe crystallizes in the orthorhombic $CeCu_2$-type structure (space group *Imma*, No. 74) with the atoms located at the following sites:

4 Eu atoms in 4(e) site: $0, \frac{1}{4}, z_1$; $0, \frac{3}{4}, \bar{z}$; $\frac{1}{2}, \frac{3}{4}, \frac{1}{2}+z_1$; $\frac{1}{2}, \frac{1}{4}, \frac{1}{2}-z_1$;

4 Ag and 4 Ge atoms (at random) in 8(h) site:

$0, y, z_2$; $0, \bar{y}, \bar{z}_2$; $0, \frac{1}{2}+y, \bar{z}_2$; $0, \frac{1}{2}-y, z_2$; $\frac{1}{2}, \frac{1}{2}+y, \frac{1}{2}+z_2$; $\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}-z_2$; $\frac{1}{2}, y, \frac{1}{2}-z_2$; $\frac{1}{2}, \bar{y}, \frac{1}{2}+z_2$.[16]

X-ray and neutron diffraction data indicate that the RAuGe compounds with R = La…Nd, Sm, Gd…Er crystallize in the hexagonal LiGaGe-structural type.[17] EuAuGe crystallizes in a new ordered version of the $CeCu_2$-type structure.[18]

A detailed analysis of the crystal structure of the RAuGe compounds with R = Y, La, Ce and Lu is done in Refs. 19–21. In these compounds, the Au and Ge atoms form a flat two-dimensional (2D) system with a small interlayer interaction. The interlayer bonding depends on the rare earth atoms. In the RAuGe (R = La and Ce) compounds, a two dimensional order and for R = Lu a three dimensional order is observed.

New X-ray data collected for YbAuGe show various structural modifications as a function of temperature: α – up to 1003 K, β – in the range 1003 to 1308 and γ – at $T > 1308$ K. The first two phases, *i.e.* α and β, have the orthorhombic structure related to the CaCuGe-type, while the γ-phase has the orthorhombic $CeCu_2$-type structure.[22]

New neutron diffraction data for HoAuGe and ErAuGe indicate a monoclinic distortion of the hexagonal structure at low temperatures.[23]

Stannides

The single-crystal X-ray data of LaCuSn,[24] NdCuSn, SmCuSn, GdCuSn[25] and DyCuSn[26] and the neutron diffraction data of the polycrystalline

RCuSn (R = Tb...Er) compounds[27] indicate the LiGaGe-type structure with Cu and Sn atoms located at different sites in the crystal lattice.

The RAgSn (R = Ce...Tm, excluding R = Eu and Yb) compounds crystallize in the hexagonal LiGaGe-type structure.[28] EuAgSn crystallizes in the orthorhombic $CeCu_2$-type structure[29] while YbAgSn crystallizes in CaLiSn type structure[30] (space group $P3m1$, No. 156) with the atoms at the following sites:

Yb atom in 1(a) site: 0, 0, 0.337;

Yb atom in 1(a) site: 0, 0, 0.669;

Yb atom in 1(a) site: 0, 0, 0;

Ag atom in 1(b) site: $\frac{1}{3}$, $\frac{2}{3}$, 0.1917;

Ag atom in 1(b) site: $\frac{1}{3}$, $\frac{2}{3}$, 0.811;

Ag atom in 1(c) site: $\frac{2}{3}$, $\frac{1}{3}$, 0.499;

Sn atom in 1(b) site: $\frac{1}{3}$, $\frac{2}{3}$, 0.4976;

Sn atom in 1(c) site: $\frac{2}{3}$, $\frac{1}{3}$, 0.1488;

Sn atom in 1(c) site: $\frac{2}{3}$, $\frac{1}{3}$, 0.8464.

The RAuSn (R = Pr, Nd, Gd...Ho) compounds crystallize in the hexagonal LiGaGe-type structure while those with R = Er...Lu have the cubic MgAgAs-type structure (space group $F\bar{4}3m$, No. 216) with atoms at the following sites:

4 R atoms in 4(c) site: $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$; $\frac{1}{4}$, $\frac{3}{4}$, $\frac{3}{4}$; $\frac{3}{4}$, $\frac{1}{4}$, $\frac{3}{4}$; $\frac{3}{4}$, $\frac{3}{4}$, $\frac{1}{4}$;

4 Au atoms in 4(a) site: 0, 0, 0;   0, $\frac{1}{2}$, $\frac{1}{2}$; $\frac{1}{2}$, 0, $\frac{1}{2}$; $\frac{1}{2}$, $\frac{1}{2}$, 0;

4 Sn atoms in 4(d) site: $\frac{3}{4}$, $\frac{3}{4}$, $\frac{3}{4}$; $\frac{3}{4}$, $\frac{1}{4}$, $\frac{1}{4}$; $\frac{1}{4}$, $\frac{3}{4}$, $\frac{1}{4}$; $\frac{1}{4}$, $\frac{1}{4}$, $\frac{3}{4}$.[31]

YbCuSn and YbAuSn crystallize in the orthorhombic TiNiSi type structure (space group $Pnma$, No. 62). 4 Yb, 4 T and Sn atoms occupy the 4(c) positions: x, $\frac{1}{4}$, z; $\bar{x}$, $\frac{3}{4}$, $\bar{z}$; $\frac{1}{2}-x$, $\frac{3}{4}$, $\frac{1}{2}+z$; $\frac{1}{2}+x$, $\frac{1}{4}$, $\frac{1}{2}-z$ with different values of x and z parameters.[32]

Figure 2 shows the lattice parameters a and c and the c/a ratio dependence on the number of 4f-electrons for some of the above compounds. Distinct anomalies for CeAgSn and YbAuGe are observed. Such anomalies are frequent in all the series of intermetalic compounds of Ce and Yb, for tetra- and divalency of the rare earth ion, respectively. The jump in the c-parameter value as well as in the c/a ratio for RCuGe is caused by the change of the crystal structure from the AlB_2-type to LiGaGe-type.

In Figure 3, volume per formula unit is plotted as a function of the atomic number of the 4f element. On the basis of this dependence, the following correlations could be yielded:

– the atomic volume decreases with an increase in the number of 4f electrons (La $\rightarrow$ Lu),
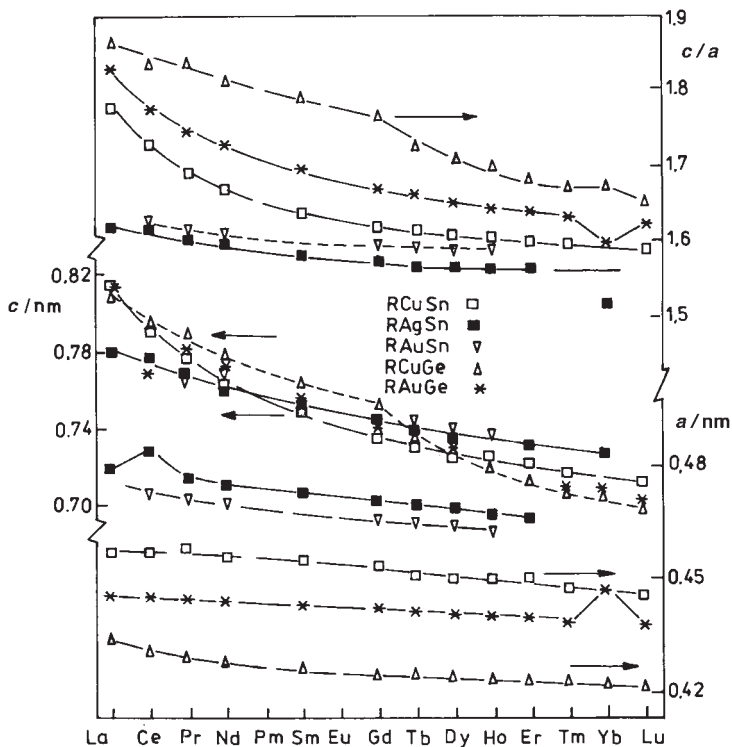
Figure 2. Composition dependence of the lattice parameters *a* and *c* and the *c/a* ratio of some RTX compounds crystallizing in LiGaGe-type (R = rare earth, T = Cu, Ag, Au, X = Sn, Ge).

– the atomic volume increases with an increase in the radius of T element (Cu → Ag → Au),

– in the RAuSn system, a jump in the atomic volume, connected with the change of the crystal structure from the hexagonal LiGaGe-type to the cubic MgAgAs-type, is observed,

– anomalous values of the unit cell volume observed for EuAgSi, Eu-CuGe, EuAgGe, RAuGe, EuCuSn, EuAgSn, YbAuGe, YbCuSn, YbAgSn and YbAuSn indicate that the rare earth ion state in these compounds differs from that of R^{3+}.

METHOD OF ANALYSIS

In this work, the crystal structure of RTX compounds where R is a rare earth metal (except for Ce, Eu and Yb), T = Cu, Ag, Au and X = Si, Ge, Sn is
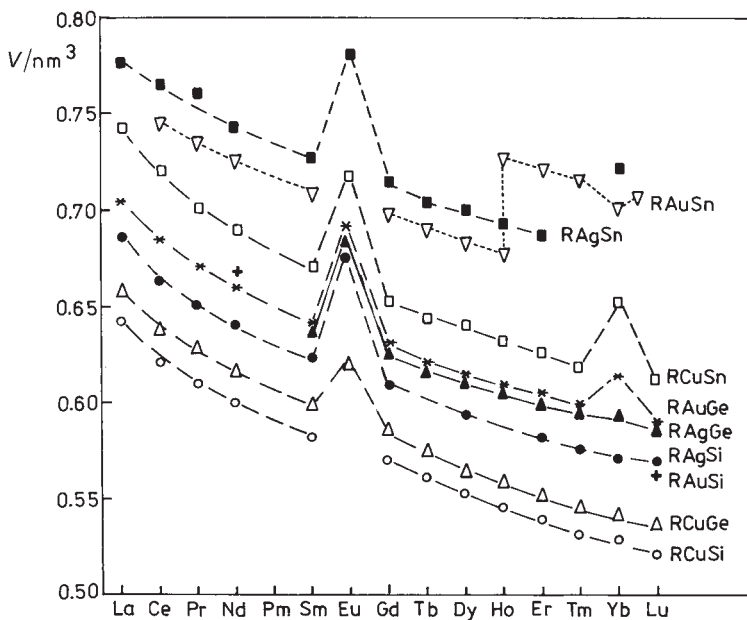
Figure 3. Volume per formula unit of RTX *vs.* the atomic number of the rare earth atom.

discussed. These compounds crystallize in five different types of hexagonal structure: disordered AlB_2-type or $CaIn_2$-type and ordered ZrBeSi-type, ZrNiAl-type and LiGaGe-type. The crystal structure data presented in Figure 1 show that the LiGaGe type crystal structure is prefered in this series of compounds. In the above listed compounds, the electron concentration is constant and equal $8/3$ (3 electrons from the rare earth atom, 1 electron from the T metal and 4 electrons form X atoms). A different type of crystal structure and the anomalies observed in the lattice parameters plot *versus* the number of 4f-electrons indicate that europium and ytterbium ions are not trivalent. ^{151}Eu Mössbauer effect data for EuAgSn indicate the stable divalent state of Eu in this compound.[29]

To clear up the difference in the crystal structure of these compounds, the analysis of chemical bonding was performed.

The analysis of chemical bonding in RTX compounds was performed on the basis of the Pearson-Villars model,[33] in which interatomic distances were analyzed in comparison with the atomic radii of atoms. For these compounds, the function:

$$\Delta_{i-j} = d_{i-j} - (R_i + R_j)$$

was determined. R_i and R_j are the atomic radii of i and j atoms, according to Vainshtein *et al.*,[34] respectively, and d_{i-j} is the interatomic distance between i- and j-atoms, obtained on the basis of experimental data.

A diagnostic parameter f_{i-j} is introduced by the following relation

$$\Delta_{i-j} = f_{i-j}\, D_R + k$$

where k is a constant. D_R is the atomic diameter of the rare earth metal.

In the ideal structure ($d_{i-j} = R_i + R_j$), a particular contact totally controls the cell dimensions ($\Delta_{i-j} = 0$ and $f_{i-j} = 0$). However, for various reasons, non-ideal situations ($d_{i-j} \neq R_i + R_j$) are generally found even though a contact totally controls the cell dimensions so that $f_{i-j} \approx 0$ and $\Delta_{i-j} \neq 0$. The value $f_{i-j} \approx 0$ indicates that the particular contacts between i and j atoms control the cell dimensions.

TABLE I

Values of the f_{i-j} parameters of RTX compounds (R = rare earth atom, T = Cu, Ag, Au, X = Si, Ge, Sn)

System	f_{R-R}		f_{R-T}		f_{R-X}		f_{T-X}		Ref.
	L	H	L	H	L	H	L	H	
RCuSi	−0.492 +1.094		0.376		0.376		0.293		20
RCuGe	non linear	+0.83	+1.2	−1.13 +0.65	−1.2	+0.5 −1.13	+0.6	−0.85	this work
RAgGe		−0.5		+0.19 +0.04		−0.1 +0.06		+0.5 +0.375	this work
RCuSn	+5.5	+0.18	+2.4 +2.2	+1.42 −4.10	−2.9 +10.3	+0.17 +0.65	−1.0	+0.43	this work
RAgSn	+2.45	−0.69	−1.5 +8.2	~0 +0.87		~0 ~0	−2.6	−0.07	this work
RAuSn	+2.0	-0.5_h	+15.1 +17.6	$+1.25_h$ -1.72_h $+0.3_c$	−0.7 +3.0	-0.57_h -1.67_h $\sim 0_c$	−2.5	$\sim 0_h$ $+0.55_c$	this work

L – light rare earth atoms, H – heavy rare earth atoms;
h – hexagonal structure, c – cubic structure.

For silicides, this calculation can be performed only for the RCuSi compounds because the crystal structure data are scarce for the others.

The values of Δ_{i-j} for RCuSi vary linearly with the atomic diameter of the rare earth atom D_R. The R–Cu, R–Si and Cu–Si bonds control the lattice parameters in the case of RCuSi and the values of Δ_{i-j} are close to zero.[35] The determined values are listed in Table I.

In Figure 4, the dependence of Δ_{i-j} on diameter D_R of the rare earth atom is shown for RTSn (T = Cu, Ag, Au), RCuGe and RAgGe series of compounds. The dependences of Δ_{R-R} on the atomic diameter D_R, shown on the top left-hand side, are different for light and heavy rare earth elements. For the RCuGe compounds, the Δ_{R-R} values are constant for R = La, Ce, Pr and then decrease down to Tm. The data presented in this figure cleary show that the Δ_{R-R} function indicates, for this system, the change of the crystal structure between GdCuGe-type and TbCuGe-type.[12]

Similar strong dependence of Δ_{R-R} on D_R is observed in the RAuGe compounds for light rare earths. There are no reliable crystal structure data for this system. The crystal structure of the RCuGe compounds is stabilized, in both phases, by the Cu–Ge distance.

For the RAgGe compounds, which crystallize in the hexagonal ZrNiAl-type of crystal structure, the rare earth atoms occupy the pyramidal 3(f) sites whereas the silver atoms occupy the tetrahedric 3(g) sites. For the ideal pyramidal coordination, the x_R parameter is given by the formula

$$x_R = \tfrac{2}{3} - \tfrac{1}{4}\,(c/a)^2$$

whereas for tetrahedric site it is

$$x_T = \tfrac{1}{3} - \tfrac{1}{4}\,(c/a)^2$$

A comparison between experimental values and those calculated using the above formula[14] is given in Table II. They are in good agreement for tetrahedric positions while for pyramidal positions the values obtained experimentally are greater than the calculated ones. It is possible to determine the interatomic distance for R–Ag and Ag–Ge because the interatomic distances are functions of the c/a ratio:

$$d_{R-Ag} = (\tfrac{1}{3} + \tfrac{1}{4}\,(c/a)^2)a,$$

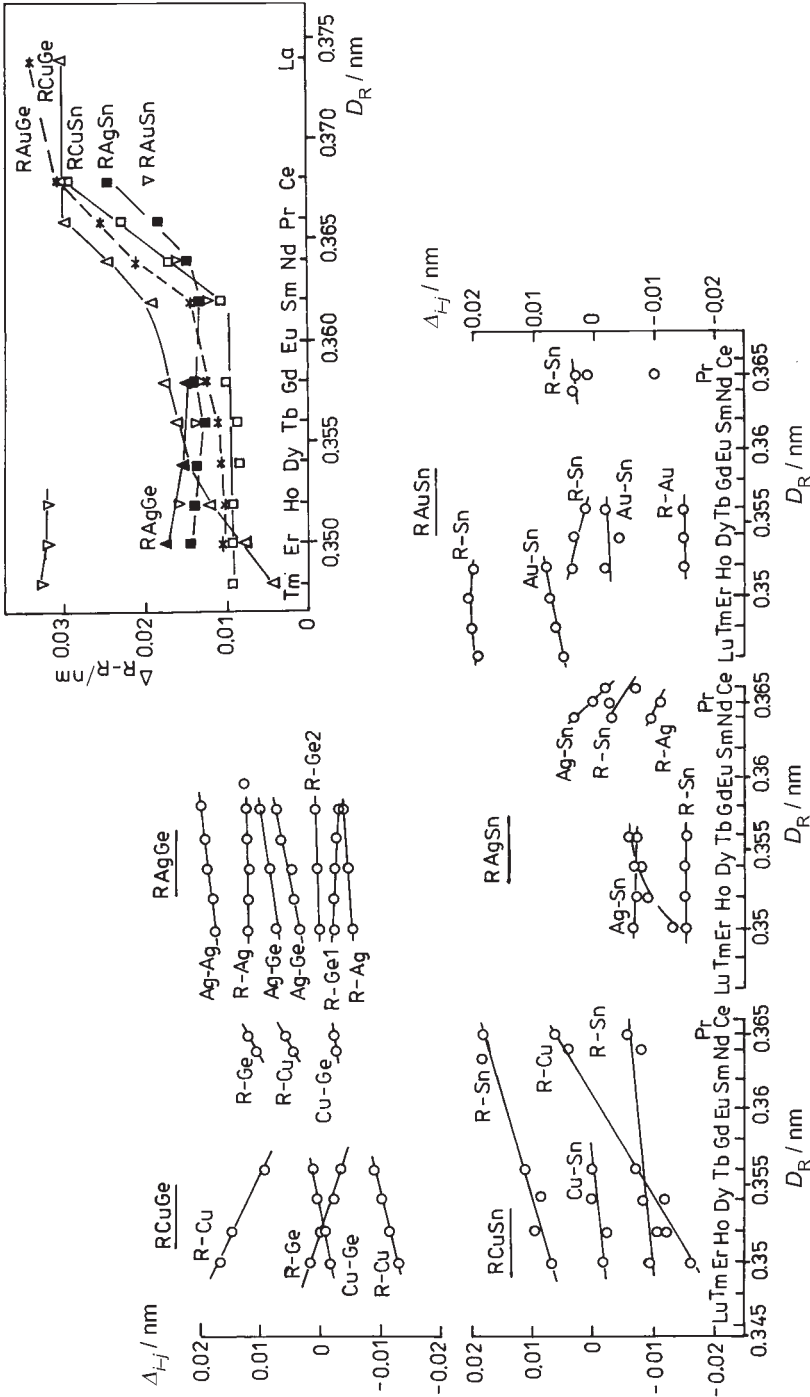$$d_{Ag-Ge} = (1/9 + 1/16\,(c/a)^4 + 1/12\,(c/a)^2)^{1/2}a.$$

Figure 4. The observed Δ_{i-j} values $vs.$ D_R plotted for RTX compounds.

TABLE II

Comparison between calculated and observed x_R and x_T parameters of RAgGe compounds

R	x_R		x_T	
	theor.	exp.	theor.	exp.
Tb	0.5794	0.5867(17)	0.2460	0.2467(34)
Dy	0.5794	0.5827(17)	0.2460	0.2492(35)
Ho	0.5794	0.5828(17)	0.2460	0.2459(39)
Er	0.5796	0.5856(15)	0.2463	0.2498(37)

The analysis of the interatomic distances in the RAgGe compounds indicates the complicated character of the chemical bonding in these compounds.

In all compounds, the Ag–Ag distances are significantly longer and do not contribute to the chemical bonding. The R–Ge interatomic distances are almost equal to the sum of atomic radii of R and Ge atoms ($\Delta_{R-Ge} \approx 0$ and $f_{R-Ge} = 0.05$). The Ag–Ge distances are larger than the sum of the atomic radii of Ag and Ge atoms ($\Delta_{Ag-Ge} > 0$ and $f_{Ag-Ge} = 0.5$). These data indicate that, in the RAgGe compounds, the R–Ge1 and R–Ge2 as well as R–Ag contacts stabilize the hexagonal ZrNiAl-type structure.

In stannides, a decrease in Δ_{R-R} versus D_R is observed for light rare earths while for heavy rare earths Δ_{R-R} slightly depends on D_R. It indicates that Δ_{R-R} controls the cell dimensions for heavy rare earth stannides. In the RAuSn compounds, a change of the crystal structure from the hexagonal LiGaGe-type to the cubic MgAgAs-type is related to an increase in the R–R distances. This change of the crystal structure is clearly visible in the modification of the value of f_{i-j} coefficients. An analysis performed for the other interatomic distances shows that the T–Sn and R–Sn distances stabilize the crystal structure in the heavy rare earth compounds with the LiGaGe-type structure.

VARIATION OF CRYSTAL STRUCTURES

In some of the RTX compounds, the change of the crystal structure is observed with variation of the atomic number of the rare earth, the transition metal as well as of the main group element. In Table III, an example of this structural change between different types of crystal structure is given. The arrows indicate the direction of the changes. The change of crystal structure is connected with a modification of interactions between different atoms.

TABLE III

Changes in the crystal structure type observed for the ternary equiatomic RTX compounds (R = rare earth atom, T = Cu, Ag, Au, X = Ge, Sn)

LiGaGe	CaIn$_2$	AlB$_2$	ZrNiAl	MgAgAs

Change with increasing atomic number of the rare earth element

| RCuGe (Tb...Lu) | $\rightarrow$ | RCuGe(La...Gd) | | |
| RAuSn (Pr...Ho) | $\rightarrow$ | | | RAuSn (Er...Lu) |

Change with increase in period number of transition element

| RCuGe (Tb...Lu) | $\rightarrow$ | | RAgGe (Gd...Er) | |
| RAgSn (Er...Lu) | $\rightarrow$ | | | RAuSn (Er...Lu) |

Change with increase in period number of main group element

| | RCuSn (Pr,Nd) $\leftarrow$ RCuGe (Pr,Nd) | | | |
| RAgSn (Gd...Er) | $\leftarrow$ | | RAgGe (Gd...Er) | |

According to the prediction of Senateur *et al.*,[36] the interactions between the rare earth (R) and transition metal (T) elements play the main role in the structural changes while, as noted by the Miedema theory,[37] the strength of the bond between R and T elements depends on the T atom group number.
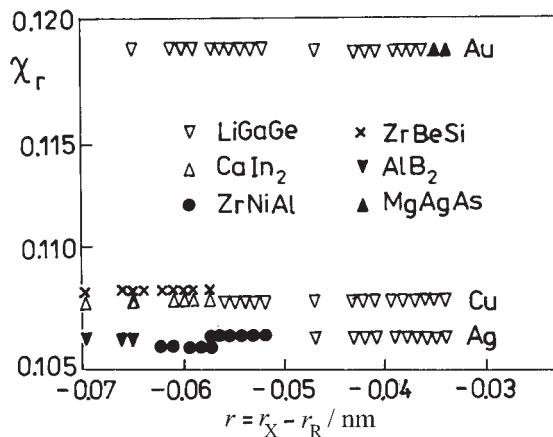

Figure 5. Two-dimensional scheme of crystal structures found in RTX compounds; electronegativity χ_r of the T element (T = Cu, Ag, Au) *vs.* the atomic radii ($r = r_X - r_R$) is shown.

The analysis of the observed phase transitions in RTX compounds (where R = rare earth elements, T = Cu, Ag, Au and X = Si, Ge, Sn) is performed on the basis of the two-dimensional structural scheme.[38] The coordinates are provided by a combination of atomic radii, as $r = r_X - r_R$, and the electronegativity χ_r of the T element according to the Martynov and Batsanov values.[39] The obtained two-dimensional structural scheme is shown in Figure 5. For the large difference between the radii of R and X elements and small values of electronegativity, different types of hexagonal structures are observed. In the case of large values of both of the above parameters, the LiGaGe-type structure is stabilized. For small values of r and large values of electronegativity, the cubic MgAgAs-type structure is observed.

ELECTRONIC STRUCTURE

The data concerning the electronic structure of the RTX compounds are obtained from:

– calculation of electronic structure,
– XPS photoelectron spectra,
– electrical resistivity,
– electronic part of specific heat,
– magnetic measurements.

Calculations of the electronic structure were performed for RAuGe (R = Sc, La, Ce, Lu)[20,21] and RAgSn (R = Ce, Dy)[40] compounds.

In RAuGe compounds, the Ge s-bands are found at about 10 to 12 eV while Au d-band between 5 and 7 eV below the Fermi level E_F. For CeAuGe, the 4f-bands are found at E_F and 1 eV above it.[20,21]

In RAgSn (R = Ce, Dy) compounds, the Sn s-bands are found at 7.5 eV while Ag d-bands is 5.5 eV below E_F. Ce 4f-band is near the Fermi level while Dy 4f-level is 4.5 eV below E_F[40].

The XPS fotoelectron spectra were collected for CeAgSn and DyAgSn, only.[41] The obtained positions of particular bands are in good agreement with the calculated data[40] presented above.

The electronic structure and bonding of some ternary AlB_2-type compounds ATX (A $\equiv$ 2a, T $\equiv$ transition metal, X $\equiv$ 5b-element) were studied by means of Extended Hückel and TB-LMTO-ASA calculations.[42] In a simple orbital interaction scheme, based on local symmetry, band structures of the compounds crystallizing in the ZrBeSi-type structure are described. The d-band of the transition element is close to the Fermi level.

The temperature dependence of the electrical resistivity gives:

– for RAuGe compounds, ρ is almost temperature independent for R = Sc and Lu while a clear linear dependence is observed for R = Y, La[21] and Ce[19],

– for RAgSn (R = Ce, Dy)[42] and RCuSn (R = Gd, Dy, Ho)[27] compounds, a the linear dependence $\rho(T)$ typical of metallic conductivity is observed.

From the low temperature part of the specific heat of RAuGe compounds, the electronic specific heat coefficient γ is determined.[21] For the compounds with R = Sc, Y, La and Lu, γ value is close to 2.50(2) mJ mol^{-1} K^{-2}. The values of the electronic specific heat coefficient γ in Ce compounds are different. For CeCuX (X = Si, Ge and Sn), they are 65 (X = Si), 13 (X = Ge) and 32 mJ mol^{-1} K^{-2} (X = Sn),[43] respectively, while for CeAgGe 15.7 mJ mol^{-1} K^{-2}.[15] Large values of γ are observed in CeAuSn (270 mJ mol^{-1} K^{-2}) and CeAgSn (210 mJ mol^{-1} K^{-2}).[44] The γ coefficient is proportional to the electronic densities of states $N(E_\mathrm{F})$ at the Fermi level. The value of the γ coefficient for CeAgSn is in good agreement with the observed and the calculated electronic structure of this compound.

Magnetic measurements indicate that, in the majority of these compounds, the magnetic moment is localized on the rare earth atoms and the values of effective magnetic moments are close to the free R^{3+} ion values. These results suggest that the rare earth atoms are electropositive and transfer three electrons to the conduction band.

In the case of compounds with the non magnetic component R = Y, La, Lu, the temperature-independent magnetic susceptibility is observed.[21] This is connected with the conduction electron distributions (Pauli susceptibility) and indicates the absence of the magnetic moment on the T transition metal.

CONCLUSIONS

The analysis of the crystal structure and the interatomic distances of RTX intermetallic compounds with R = rare earth metal, T = Cu, Ag, Au and X = Si, Ge, Sn leads to the following conclusions:

– the majority of these compounds crystallize in the hexagonal LiGaGe-type structure stabilized by a particular value of the valence electron concentration (VEC = $\frac{8}{3}$),

– the different type of crystal structure and the large unit cell volume for Eu and Yb compounds indicate a probable divalent state for europium and ytterbium ions in these compounds (VEC = $\frac{7}{3}$),

– the direct contact between different atoms controls the lattice parameters,

– the large difference between the radii of rare earth and X (Si, Ge, Sn) elements or large difference in the electronegativities of X elements (X = Cu, Ag, Au) determine different types of the crystal structure. The above data indicate the complicated nature of chemical bonding. Geometrical and electronic factors play their respective parts in the stability of the crystal structure.

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SAŽETAK

Strukturni aspekti kemijskog vezivanja u intermetalnim spojevima opće formule RTX

Andrzej Szytuła

Dimenzije jedinične ćelije ternarnih intermetalnih spojeva formule RTX (R je element iz skupine rijetkih zemalja, T je prijelazni element, a X su Si, Ge ili Sn) analizirane su s obzirom na polumjer atoma elementa rijetke zemlje. Na osnovi podataka o kristalnoj strukturi ponuđena je informacija o kemijskom vezivanju u ovih faza.