

論文 / 著書情報  
Article / Book Information

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## 論文要旨

THESIS SUMMARY

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要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words )

In drawing from elements across the periodic table, intermetallic systems sample a wide range of bond polarities and degrees of electron localization. It is why intermetallic phases represent diversity of bonding interactions. Many researchers have studied to find a kind of rule to distinguish a complicated chemical bonding theory in intermetallics. Chemical bonding theory is established from a view of relation between crystal structure and electron count, because stable structure makes Fermi level lie in the pseudo-gap. The conventional Hume-Rothery phases are considered in terms of a weakly-perturbed free-electron gas. On the other hands, Zintl phases and transition metal-main group ( $18-n$  rule) intermetallics are extended from octet rule and  $18-n$  rule organometallic compounds, respectively.

In this thesis, bonding analysis of CaCu, and Ca<sub>2</sub>Cu was performed as a challenge to clarify a bonding nature of electropositive metal-transition metal polar intermetallics, using reversed approximation Molecular Orbital (raMO) analysis. The electronic structures of CaCu and Ca<sub>2</sub>Cu can be simply separated into Ca- and Cu-centered components. This feature can be considered that the number of valence electrons of CaCu and Ca<sub>2</sub>Cu is not enough to make noble gas electron configuration for Cu, reading to electron distribution of not only anion clustering but also cation clustering. This is contrast to the transition metal isolobal bonds that form in other intermetallics with the support of bridging contributions from p-block elements, such as Sn, Ga, or Al.

Furthermore, ZrCuSiAs-type LnCrAsO (Ln = La, Ce, Pr, and Nd), La<sub>2</sub>Fe<sub>2</sub>Se<sub>2</sub>O<sub>3</sub>-type La<sub>2</sub>Cr<sub>2</sub>As<sub>2</sub>O<sub>y</sub>H<sub>x</sub>, and ZrNiAl-type ScRuX (X = Si, Ge) are considered from a view of effect of addition of electronegative main group element in electropositive metal-transition metal. The addition of more electronegative main group element increase the number of valence electrons and shift the intermetallic system from polar intermetallics to  $18-n$  rule intermetallic phases.

In the chapter 2, I have examined the chemical bonding of CaCu and Ca<sub>2</sub>Cu underlying the tendency of electropositive metal atoms to cluster in the structures of intermetallic phases. The atomic packing in both Ca<sub>2</sub>Cu and its parent CaCu phase is suggestive of a segregation of Ca-Cu and Ca

domains, being built from Ca-capped Cu-Cu chains and blocks of close-packed Ca atoms. raMO analysis supports this viewpoint in its division of the electronic structure into (1) essentially single-bonded Cu-Cu chains supported by bridging Ca atoms, (2) electrons delocalized over the Ca sublattice that can be organized into variety of resonance structures with one electron occupying each  $\text{Ca}_4$  tetrahedron, on average. Implicit in these results is a chemical story related to electronegativity: the Cu sublattices in these structures do not have a sufficient number of low-lying orbitals to completely oxidize the Ca atoms to  $\text{Ca}^{2+}$ . In particular, the raMO analysis shows only minor involvement of bonding interactions between Cu 4p orbitals, despite the availability of Ca bridging atoms.

In the chapter 3, I presented the crystal and magnetic structure of Cr-based layered oxyarsenide  $\text{LaCrAsO}$  determined by X-ray and neutron powder diffraction measurements.  $\text{LnCrAsO}$  ( $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{and Nd}$ ) were successfully synthesized by solid state reactions.  $\text{LaCrAsO}$  is an early end member of  $\text{LaTAsO}$  family. In the case of the center of this family is  $\text{LaFeAsO}$ , there are  $3 + 8 + 5 + 6 = 22$  electrons/formula unit. Among them, 8 electrons/formula unit are used to fill O 2s and 2p orbitals. Left 14 electrons/formula unit can be considered to analyze Fe-Fe bonding. Fe are formed square net in this phase, therefore, the number of Fe-Fe is 4. The  $18-n$  rule can support the phase stability of  $\text{LaFeAsO}$ . Failure to synthesize  $\text{LaCrPO}$  and  $\text{LaCrSbO}$  is one of clue of stability is originated from electron count. Magnetic and electrical property measurements revealed that  $\text{LaCrAsO}$  is a metal with G-type magnetic structure with the Cr spin parallel to its c-axis. Itinerant AFM similar to that of  $\text{LaFeAsO}$ , which is the parent compound of Fe-based high  $T_c$  superconductors, was observed for  $\text{LaCrAsO}$  but its magnetic order differed, with a high magnetic moment of  $1.57 \mu_B$  at RT. The temperature dependence of magnetic susceptibility of  $\text{LaCrAsO}$  also showed a broad hump at  $\sim 550$  K indicating AFM with a Neel temperature below 550 K. Metal-insulator transition was observed for  $\text{LaCrAsO}$  upon electron-doping by Mn-substitution of the Cr sites.

In the chapter 4, in conclusion, a range new oxyhydrides  $\text{La}_2\text{Cr}_2\text{As}_2\text{O}_y\text{H}_x$  ( $0.1 < y < 1.6$ ) with 2223-type layered structure were synthesized by hydride doping of the 1111-type  $\text{LaCrAsO}$  compound. The structural change from  $\text{LaCrAsO}$  to  $\text{La}_2\text{Cr}_2\text{As}_2\text{O}_y\text{H}_x$  involves features: (1) A slip occurs along slip plane (001) in the direction [110]. (2)  $\text{H}^-/\text{O}^{2-}$  anions are incorporated into the  $\text{Cr}_2\text{As}_2$  layers, changing the coordination number of Cr from 4 to 6. (3) Extra  $\text{H}^-/\text{O}^{2-}$  ions are inserted into the  $\text{Cr}_2\text{As}_2$  layers, suppressing the reduction of Cr ion that would occur for simple  $\text{H}^-/\text{O}^{2-}$  substitution within the original 1111-type structure. In this way, we see how hydride substitution in the 1111-type can do more than simply provide conventional electron doping; it can also drive changes in the local coordination structure around the transition metal sites.

In the chapter 5, hydrogenation of nitrobenzene were conducted using ScRuX (X = Si and Ge) ternary intermetallics as catalysts, to investigate how different p-block elements between Si and Ge affect chemical reaction. ScRuGe, which is chemically stable and effective for hydrogenation of nitrobenzene, showed ca. 9 times higher turnover frequencies than ScRuSi, even the difference of electronegativity is quite small between Ge and Si. ScRuGe showed good chemoselectivity for nitro-group.

備考：論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note : Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1copy of 800 Words (English).

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