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論文 / 著書情報
Article / Book Information

題目(和文)	
Title(English)	Chemical Bonding of CaCu, Ca2Cu, and Related Intermetallics
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出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第11286号, 授与年月日:2019年9月20日, 学位の種別:課程博士, 審査員:細野 秀雄,松石 聡,神谷 利夫,平松 秀典,北野 政明,多田 朋史
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第11286号, Conferred date:2019/9/20, Degree Type:Course doctor, Examiner:,,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

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（博士課程）
Doctoral Program

論文要旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	材料　系 材料　コース	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of　（　工学　）
学生氏名： Student's Name	朴　相源	指導教員（主）： Academic Supervisor(main)	細野　秀雄　教授
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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_2Cu 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_2Cu 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_2Cu 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), $La_2Fe_2Se_2O_3$-type $La_2Cr_2As_2O_yH_x$, 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_2Cu underlying the tendency of electropositive metal atoms to cluster in the structures of intermetallic phases. The atomic packing in both Ca_2Cu 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 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 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 LaCrAsO determined by X-ray and neutron powder diffraction measurements. *Ln*CrAsO (*Ln* = La, Ce, Pr, and Nd) were successfully synthesized by solid state reactions. LaCrAsO is an early end member of LaTAsO family. In the case of the center of this family is 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 LaFeAsO. Failure to synthesize LaCrPO and LaCrSbO is one of clue of stability is originated from electron count. Magnetic and electrical property measurements revealed that LaCrAsO is a metal with G-type magnetic structure with the Cr spin parallel to its c-axis. Itinerant AFM similar to that of LaFeAsO, which is the parent compound of Fe-based high T_c superconductors, was observed for LaCrAsO but its magnetic order differed, with a high magnetic moment of 1.57 μ_B at RT. The temperature dependence of magnetic susceptibility of LaCrAsO also showed a broad hump at ~550 K indicating AFM with a Neel temperature below 550 K. Metal-insulator transition was observed for LaCrAsO upon electron-doping by Mn-substitution of the Cr sites.

In the chapter 4, in conclusion, a range new oxyhydrides $La_2Cr_2As_2O_yH_x$ ($0.1 < y < 1.6$) with 2223-type layered structure were synthesized by hydride doping of the 1111-type LaCrAsO compound. The structural change from LaCrAsO to $La_2Cr_2As_2O_yH_x$ involves features: (1) A slip occurs along slip plane (001) in the direction [110]. (2) H^-/O^{2-} anions are incorporated into the Cr_2As_2 layers, changing the coordination number of Cr from 4 to 6. (3) Extra H^-/O^{2-} ions are inserted into the Cr_2As_2 layers, suppressing the reduction of Cr ion that would occur for simple H^-/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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