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論文要約

論文題目

“Chemical Bonding of CaCu, Ca_2Cu, and Related Intermetallics”

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本論文の概要

The structures and stability of intermetallic phases are governed by an immense diversity of bonding interactions that has yet to be fully comprehended by chemical theory. The structures of the simplest Zintl phases are well-rationalized with the view of electrons populating covalent bonds between the anions to complete filled octets or cluster shells, while the Hume-Rothery phases are considered in terms of a weakly-perturbed free-electron gas, and a broad class of transition metal/p-block intermetallics being governed by a variation on the 18-electron rule.

In this thesis, I study the three subjects in intermetallics. First is the chemical bonding in intermetallics locating between Zintle phase and Hume-Rothery phase, CaCu and Ca_2Cu using tight-binding model based on DFT calculations. A unique cluster formation of Ca, which is not observed in neither Zintle or Hume-Rothery phases may be understood as a consequence of Cu with d^{10} electronic configuration and partial electron transfer from Ca to Cu. Second is chemical bonding in ZrCuSiAs-type compounds LaCrAsO and $La_2Fe_2Se_2O_3$-type $La_2Cr_2As_2O_yH_x$. Both are new materials I successfully synthesized. Crystal and magnetic structures are determined. A distinct change in local structure around Cr upon hydrogenation found, i.e., the coordination structure of Cr is transformed from tetrahedral to octahedral due to participation of H^- to the coordination. This change is interpreted by 18-*n* rule. The last is catalytic property of ternary intermetallics ScRuX (X = Si and Ge) for hydrogenation of nitrobenzene. ScRuGe showed 9 times higher than ScRuSi and this difference is understood in terms of electron donating of Ru as the active site.

各章の概要

Chapter 1. “General Introduction”

Chemical bonding of intermetallics are summarized; Hume-Rothery phase, Zintl phase, and 18-n rule Transition metal-main group intermetallic phase. Then, the motivations and objectives of this thesis are described.

Chapter 2. “Cation Clustering in Intermetallics: The Modular Bonding Schemes of CaCu and Ca_2Cu”

Bonding schemes of CaCu and Ca_2Cu are investigated using tight binding model based on the result of the DFT calculations. Electropositive metals, such as the alkaline earths or lanthanides, are generally assumed to act largely as spectator cations in solid state compounds. In polar intermetallic phases, atoms of such elements are indeed often placed at the peripheries of anions or polyanionic fragments. However, they also show a pronounced tendency to cluster with each other in these peripheral regions in a manner suggestive of multicenter bonding. In this chapter, I theoretically investigate the bonding schemes and driving forces that underlie these cationic cluster arrangements, focusing on CaCu (whose two polymorphs are based on the intergrowth of the FeB- and CrB-types) and Ca_2Cu (a Ca-intercalated derivative of CaCu). The structures of these phases are based on Cu zigzag chains embedded in matrices of Ca atoms arranged into increasingly well-developed fragments of closest-packed arrangements. Using reversed approximation Molecular Orbital (raMO) analysis, the Cu chains of both structure are revealed to be connected via nearly fully-occupied Cu-Cu isolobal σ bonds, such that the Cu atoms control 12 of the 13 and 15 electrons/formula unit of CaCu and Ca_2Cu, respectively. The remaining electrons are drawn to multicenter bonding functions in the Ca sublattices, despite the availability of additional Cu 4p orbitals, indicating that the electronegativity difference between Ca and Cu are insufficient to achieve formal Cu oxidation states far beyond 1-. The metallic nature of the Ca-based bonding subsystem is reflected in the raMO analysis by plurality of resonance structures can be generated from the occupied crystal orbitals. Across these bonding schemes, a separation of the electronic structure into largely self-contained Ca-Ca and Ca-Cu states is a consistent theme. This modularity in the bonding can be correlated to the ease with which this and related systems rearrange FeB- and CrB-type features, which may provide clues to identifying other intermetallic families with similar degrees of structural versatility.

Chapter 3. “Magnetic structure and electromagnetic properties of *Ln*CrAsO with ZrCuSiAs-type structure (*Ln* = La, Ce, Pr, and Nd)”

The synthesis, structure and electromagnetic properties of Cr-based layered oxyarsenides LnCrAsO (Ln = La, Ce, Pr, and Nd) with a ZrCuSiAs-type structure are studied. All LnCrAsO samples showed electronic conduction. Electron doping in LaCrAsO by Mn-substitution for the Cr sites gave rise to a metal-insulator transition. Analysis of powder neutron diffraction data revealed that LaCrAsO had G-type antiferromagnetic (AFM) ordering, i.e., checkerboard-type AFM ordering in the CrAs plane and antiparallel spin coupling between the adjacent CrAs planes, at 300 K with a large spin moment of 1.57 μ_B along the c-axis. The magnetic susceptibility of LaCrAsO was very small (the order of 10^{-3} emu/mole) and showed a broad hump at ~550 K. First-principles density-functional theory calculations of LaCrAsO explained its crystal structure and metallic nature well, but could not replicate the antiparallel spin coupling between the CrAs layers. The stability of LaTAsO family is described using 18-*n* rule.

Chapter 4. “Transformation of chromium coordination environment in LaCrAsO induced by hydride doping : The formation of $La_2Cr_2As_2O_yH_x$”

In this chapter, I studied the synthesis of $La_2Cr_2As_2O_yH_x$ ($0.1 < y < 1.6$) oxyhydrides solid solutions using solid state reaction under high pressure with solid state hydrogen source. This system is an example of how H^- doping can also promote structural changes: H^- doping in LaCrAsO results in the formation of $La_2Cr_2As_2O_yH_x$ with the $La_2Fe_2Se_2O_3$-type layered structure. Remarkably, this transformation includes a change of the coordination number of Cr from 4 to 6, with the some of the H^- being accommodated in new sites within the CrAs layers. In this way, H^- serves not only a conventional electron dopant by substitution of O^{2-}, but also makes new bonds to the transition metals. The hydrogen defect of $La_2Ti_2As_2H_{2.3}$ and $La_2Cr_2As_2O_{0.1}H_{2.4}$ is discussed in a manner of 18-*n* rule.

Chapter 5. “Control Hydrogenation of Nitrobenzene using Ternery Intermetallic Catalyst containing Silicon and Germanium”

To investigate how different p-block elements between Si and Ge affect to hydrogenation of nitrobenzene using ScRuX (X = Si and Ge) ternary intermetallics as catalysts were conducted. 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.

Chapter 6. “General Conclusion”

The results of this thesis are summarized and future perspective is described.

Publication lists

Papers included in the thesis

1. **S. Park**, H. Hosono, D. C. Fredrickson

“Cation Clustering in Intermetallics: The Modular Bonding Schemes of CaCu and Ca_2Cu”

Inorganic Chemistry 58, 10313 (2019).

2. **S. Park**, H. Mizoguchi, H. Hiraka, K. Ikeda, T. Otomo, H. Hosono

“Magnetic structure and electromagnetic properties of *Ln*CrAsO with ZrCuSiAs-type structure (*Ln* = La, Ce, Pr, and Nd)”

Inorganic Chemistry 52, 13363 (2013).

3. **S. Park**, H. Mizoguchi, H. Hiraka, K. Ikeda, T. Otomo, H. Hosono

“Transformation of chromium coordination environment in LaCrAsO induced by hydride doping : The formation of $La_2Cr_2As_2O_yH_x$”

Inorganic Chemistry 56, 13642 (2017).

Other Papers

1. B. Cho, J. Yoon, M. G. Hahm, D. Kim, A. Kim, Y. H. Kahng, **S. Park**, Y. Lee, S. Park, J. Kwon, C. S. Kim, M. Song, Y. Jeong, K. Nam, H. C. Ko.

“Graphene-based gas sensor: metal decoration effect and application to a flexible device”

Journal of Materials Chemistry C 2, 5280 (2014).

2. H. Mizoguchi, **S. Park**, H. Hiraka, K. Ikeda, T. Otomo, H. Hosono

“New $LaMAsH_x$ (M = Co, Ni, or Cu) Arsenides with Covalent M–H Chains”

Journal of the American Chemical Society 136, 17390 (2014).

3. H. Mizoguchi, **S. Park**, H. Hiraka, K. Ikeda, T. Otomo, H. Hosono

“An Anti CuO_2-type Metal Hydride Square Net Structure in $Ln_2M_2As_2H_x$ (Ln= La or Sm, M= Ti, V, Cr, or Mn)”

Angewandte Chemie 127, 2975 (2015).

4. A. Kim, Y. Kim, J. Nam, H. Chung, D. J. Kim, J. Kwon, **S. Park**, J. Park, S. Y. Choi, B. H. Lee, J. H. Park, K. H. Lee, D. Kim, S. M. Choi, P. M. Ajayan, M. G. Hahm, B. Cho

“Alloyed 2D metal–semiconductor atomic layer junctions”

Nano letters 16, 1890 (2016).

5. B. Cho, A. Kim, D. J. Kim, H. Chung, S. Y. Choi, J. Kwon, **S. Park**, Y. Kim, B. H. Lee, K. H. Lee, D. Kim, J. Nam, M. G. Hahm

“Two-dimensional atomic-layered alloy junctions for high-performance wearable chemical sensor”

ACS applied materials & interfaces 8, 19635 (2016).

6. H. Mizoguchi, **S. Park**, T. Honda, K. Ikeda, T. Otomo, H. Hosono

“Cubic Fluorite-Type CaH_2 with a Small Bandgap”

Journal of the American Chemical Society 139, 11317 (2017).

Presentation lists

International Presentation

1. **S. Park**, H. Mizoguchi, H. Hiraka, K. Ikeda, T. Otomo, H. Hosono (Poster)

“Transformation of chromium coordination environment in LaCrAsO induced by hydride doping : The formation of $La_2Cr_2As_2O_yH_x$”

Solid-state Chemistry and Ionics workshop (The 5th SCI workshop), Sep. 10 – 13, Fukuoka, **Japan** (2018).