

Materials research utilizing hydride and metal element anions

Associate Professor Satoru Matsuishi



For the conventional ionic solid materials including transparent electrical conductors, magnets, ferroelectrics and phosphors, their active properties mainly originate from the nature of positive ions (cations) of metal elements such as transition metal and rare-earth elements. On the other hand, the role of negative ions (anions) like oxygen was prone to be neglected in most of studies.

In recent years, our research group has developed the material design concept utilizing the active anions confined in the nanometer-sized space built in materials. For example, we focus on negatively charged state of hydrogen H^- , while it has been believed that hydrogen always forms cation H^+ in ionic system. By using hydrogen as mono-valent anion in place of fluoride ion F^- substituting O^{2-} , the high concentration electron doping was achieved for oxy-arsenide $LnFeAsO$ ($Ln =$ rare-earths), the parent compounds of iron-based superconductors (Figure 1).[1] This result demonstrate that H^- can be used as electron donor in oxide materials ($O^{2-} \rightarrow H^- + e^-$). In other case, we found the superconductivity in a $p\pi-p\sigma$ bonding system of metal element anions just like those in MgB_2 and graphite intercalated compounds. In Ca_2InN , the arrays of indium chains $-(In)_n^-$ are sandwiched by $[Ca_2N]^+$ layers which are building blocks of 2-dimentional electride Ca_2N (Figure 2).[2] Due to the highly cationic property of Ca_2N layer, indium forms negative ion In^- with $6s^26p^2$ state while the typical charged state of indium (In) is +3 with $6s^06p^0$ state. The $6p$ orbitals occupied by the additional electrons make major contribution to the formation of superconducting state.

The substitution of hydride and the insertion of metal element anion will be key techniques to convert ubiquitous element compounds to novel electronic materials.

[1] S. Iimura, S. Matsuishi, H. Sato, T. Hanna, Y. Muraba,

S-W. Kim, J-E. Kim, M. Takata and

H. Hosono, *Nat. Commun.* **3**, 943 (2013).

[2] S-H. Jeong, S. Matsuishi, K-M. Lee, Y. Toda, S-W. Kim and H. Hosono, *Supercond. Sci. Technol.* **27**, 055005 (2014)

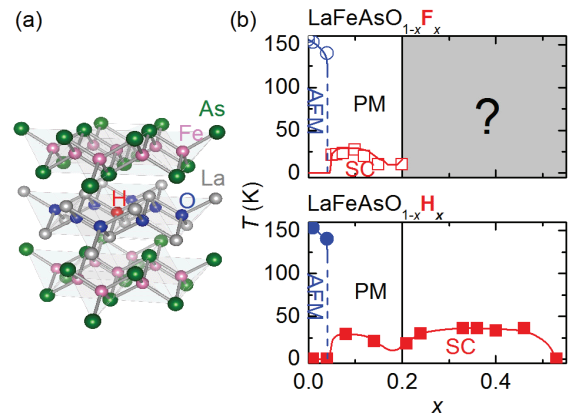


Figure 1. Hydrogen substitution to LaFeAsO. (a) Crystal Structure of LaFeAsO. (b) Electronic Phase diagrams of $LaFeAsO_{1-x}F_x$ and $LaFeAsO_{1-x}H_x$ systems (PM: paramagnetic metal, AFM: antiferromagnetic metal, SC: superconductor)

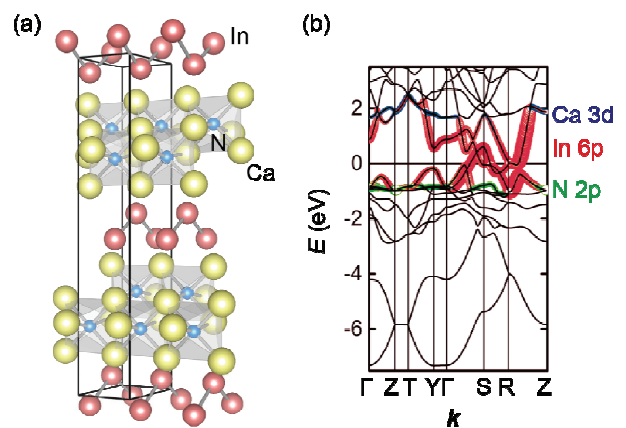


Figure 2. Ca_2InN superconductor (a) Crstal structure composed of anionic indium layer $-(In)_n^-$ is sandwiched by $[Ca_2N]^+$ cationic layers. (b) Band Structure. Electronic state located around Fermi level ($E = 0$) are mainly composed of In $6p$ orbitals.