The understanding of the fundamental nature of a material’s superconducting state is of crucial importance, if superconductors are to fulfill their promise for widespread use in energy-related needs. This talk focuses on the structural features, and the local electronic and structural components that may give clues for the causes of the superconducting state. Our research (a) involves synthesis novel correlated materials, and (b) concerns a strong characterization effort for advancing the understanding of known iron-based superconductors (FeSC). A few of our publications from 2013 and 2014 will be highlighted [1-6] on the exploratory synthesis of materials with FeSC-like structural features, the undoped parents, and the role of microscopic structural, chemical, and electronic non-uniformity for understanding the bulk collective superconducting state.

Superconductivity in the Hypervalent Compound $\text{Ba}_2\text{Bi}(\text{Sb}_{1-x}\text{Bi}_x)_2$ with a Square-Honeycomb Lattice

T. Yajima$^{1,2,*}$, F. Takeiri$^2$, Y. Nozaki$^2$, Z. Li$^3$, T. Tohyama$^{2,4}$, M. A. Green$^5$, Y. Kobayashi$^2$, and H. Kageyama$^2$

($^1$The University of Tokyo, $^2$Kyoto University, $^3$California State University Northridge, $^4$Tokyo University of Science, $^5$National Institute of Standards and Technology)

To date, in-depth and comparative studies of layered superconductors have been mostly devoted to simple and symmetric lattices such as the square lattice, the honeycomb lattice, and the triangular lattice. Exploring layered compounds with a unique structural geometry is important to finding novel exotic superconductors. There are a number of superconductors with $p$-block element networks that satisfy Zintl–Klemm (ZK) electron counting rules. In the superconductors based on light $p$-block elements such as MgB$_2$, the superconducting layer is exclusively restricted to the honeycomb lattice owing to the strong $sp^2$ hybridization of light $p$-block elements. In sharp contrast, heavy $p$-block elements such as Sb and Te are characterized by weak $s$–$p$ hybridization, providing the ability to form zigzag-based anion networks. Furthermore, some compounds adopt a hypervalent state, a state that does not follow the ZK rules, allowing for the heavy $p$-block elements to form unique geometries.

We studied the structural and physical properties of the hypervalent system $\text{Ba}_2\text{Bi}(\text{Sb}_{1-x}\text{Bi}_x)_2$ ($0 \leq x \leq 1$). The $\text{Bi}(\text{Sb}_{1-x}\text{Bi}_x)_2$ layer is anisotropic and may be viewed as an intergrowth structure of square chains and honeycomb chains, which we call a “square–honeycomb” lattice (Figure 1). We found that the orthorhombic $\text{Ba}_2\text{BiSb}_2$ ($x = 0$) shows a charge density wave (CDW) transition at approximately 230 K accompanied by a significant elongation of the $b$-axis, indicating the quasi-one-dimensional nature along the $b$-axis in its electronic state, as supported by first-principles calculations. This CDW transition is rapidly suppressed with increasing $x$, leading to the appearance of superconductivity for $0.375 \leq x \leq 1$. The superconducting transition temperature $T_c$ increases slightly with $x$ and the maximum $T_c$ was 4.4 K for $\text{Ba}_2\text{Bi}_3$ ($x = 1$) [1].


Figure 1. (a) Crystal structures of $\text{Ba}_2\text{Bi}_3$, where green, purple, and yellow spheres represent Ba, Bi(1), and Bi(2), respectively. In $\text{Ba}_2\text{Bi}(\text{Sb}_{1-x}\text{Bi}_x)_2$, the Sb atoms are positioned at the Bi(2) site. (b) [001] projection of “square-honeycomb” plane.
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Resistive Superconducting Transition and Stability at the Atmosphere in the Intercalation Superconductor $A_x(C_2H_8N_2)_yFe_{2-z}Se_2$ ($A = \text{Li, Na}$)


(Department of Applied Physics, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan)

We have succeeded in observing zero-resistivity in our newly discovered intercalation superconductors $A_x(C_2H_8N_2)_yFe_{2-z}Se_2$ ($A = \text{Li, Na}$) with $T_c = 45$ K [1,2], using pellet samples sintered at 170°C in an evacuated or argon-filled glass tube. As shown in Fig.1, it has been found that the sintered pellet samples show a metallic temperature-dependence of $\rho$ and that $T_c^{\text{zero}}$ is ~ 32 K and ~ 12 K for $A = \text{Li and Na}$, respectively. For both $A = \text{Li}$ and $\text{Na}$, $T_c^{\text{mid}}$ is ~ 42 K and almost the same as $T_c$ obtained from the $\chi$ measurements.

In order to investigate the stability of the lithium- and EDA-intercalated pellet samples at the atmosphere, they have been exposed to the atmosphere up to 7 days. From the x-ray diffraction analysis, it has been found that the crystal structure of $\text{Li}_x(C_2H_8N_2)_yFe_{2-z}Se_2$ is maintained at the atmosphere at least up to 7 days, though the $c$-axis lengths of the samples exposed for 2 - 7 days are a little larger than that of the as-intercalated sample. From the $\chi$ measurements, it has been found that the superconductivity is maintained at least up to 7 days, though both $T_c$ and the superconducting volume fraction gradually decrease. From the $\rho$ measurements of the sintered pellet samples, moreover, it has been found that zero-resistivity is maintained at least up to 5 days, though the value of $\rho$ in the normal state gradually increases. In conclusion, $\text{Li}_x(C_2H_8N_2)_yFe_{2-z}Se_2$ is comparatively resistive to the atmosphere and comparatively suitable for the application.


Fig. 1. Temperature dependence of the electrical resistivity, $\rho$, for (a) the sintered (170°C, 30 h, vacuum) pellet sample consisting of $\text{Li}_x(C_2H_8N_2)_yFe_{2-z}Se_2$ and $\text{FeSe}$, and (b) the sintered (170°C, 20 h, vacuum) pellet sample consisting of $\text{Na}_x(C_2H_8N_2)_yFe_{2-z}Se_2$ and $\text{FeSe}$. Insets show the temperature dependence of $\rho$ around $T_c$. 
Superconducting properties of iron-based superconductors 
(Ca,RE)FeAs₂

Hiraku Ogino 1*, Hiroyuki Yakita 1, Alberto Sala 1, Tomoyuki Okada 1, Akiyasu Yamamoto 1, Kohji Kishio 1, Tetsuya Tohei 1, Yuichi Ikuhara 1, Yoshito Gotoh 2, Hiroshi Fujihisa 2, Kunimitsu Kataoka 2, Akira Iyo 2, Hiroshi Eisaki 2, Jun-ichi Shimoyama 1

(1 The University of Tokyo, 
2 National Institute of Advanced Industrial Science and Technology)

Since 2008, series of iron-based superconductors such as REFeAsO (RE: rare earth), AFe₂As₂, FeSe have been developed. The structure of iron-based superconductors are composed of FeAs(FeSe, FeP etc.) layer and blocking layers, and it is important to find new kinds of blocking layers to understand mechanism of iron-based superconductors as well as enhance superconducting properties. Recently new iron-based superconductor (Ca,RE)FeAs₂ have been discovered[1]. The compounds show superconductivity above 40 K, and relatively low anisotropy is reported[2]. Crystal structure of the (Ca,RE)FeAs₂ is composed of Ca(RE) planes, Fe₄As₂ layer and As₂ layer. In As₂ layer of (Ca,Pr)FeAs₂, closest As-As distance is ~2.60 Å, suggesting existence of two As-As bonding for each As atom. Thus, As atoms form catenative chain like structure as shown in the figure, and the catenation is the first example in iron-based superconductors. Discovery of this compound proved variety of blocking layers as well as arsenic chemistry, and may bring new features in iron-based superconductors. In this presentation superconducting properties and recent progress of (Ca,RE)FeAs₂ and related topics will be presented.


Fig. 1: Crystal structure of (Ca,RE)FeAs₂(a) and top view of the As₂ chain(b)