論文 / 著書情報
Article / Book Information

題目(和文)	鉄、マンガン基四面体配位化合物の新物質と不純物効果
Title(English)	New Materials and Impurity Effect in Tetrahedral Fe, Mn Based Compounds
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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10835号, 授与年月日:2018年3月26日, 学位の種別:課程博士, 審査員:細野 秀雄,川路 均,平松 秀典,松石 聡,神谷 利夫
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第10835号, Conferred date:2018/3/26, 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

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

専攻： Department of	材料物理科学 専攻	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of （ 工学 ）
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Iron based superconductor (FeSC) is one of the greatest treasure in the condensed matter physics. The discovery of the high temperature superconductivity in the electron-doped $LaFeAsO_{1-x}F_x$ triggered the intensive research on the iron pnictides or chalcogenide. Although a number of FeSCs with various chemical compositions have been discovered at present, they commonly adopt the edge-sharing tetrahedral structure. With some exceptions, the parent phase is antiferromagnetic (AFM) semimetal. The carrier doping, isovalent doping, and pressure applying breaks the magnetic order, and then the superconductivity emerges. At the early stage of the research about FeSC, theorists suggested that the superconductivity was mediated by spin fluctuation, where paired superconducting electrons involved the sign reversal of the phase of the wave function (called $s_{\pm}$ wave state). On the other hand, orbital fluctuation scenario was also proposed which mediated the superconductivity without the sign reversal (s_{++} wave state). Despite the intensive research, however, the origin of the superconductivity still remains controversial.

To address the conundrum from the point of material synthesis, we focused on the impurity effect in several FeSCs. These two theories predict the contrastive behavior of FeSC by impurity substitution; *i.e.*, the $s_{\pm}$ wave state is susceptible to the nonmagnetic impurity which suppresses the superconductivity, whereas the s_{++} wave state is robust to the impurity effect. Therefore, we firstly performed the zinc-substitution on $LaFeAsO_{1-x}H_x$ with different H contents (x = 0.10, 0.35). Contrary to expectations, the determination of the paring symmetry was not achieved because the Anderson localization effect broke the superconductivity. Second, the cobalt-substitution on the self-doped FeSC $KCa_2Fe_4As_4F_2$ was conducted. The substitution of Co ion is expected to induce the disorder and

additional electrons in the system. Comparing the physical property with the disorder-free FeSC with the same electron count, we observed the effect of disorder in FeSC. That is, the disorder suppressed not only the superconductivity but also the magnetic ordering even though the spin density wave transition was expected.

Beyond the research about FeSC, we expanded our research area to the other types of tetrahedral compounds. The principal aim was to discover new superconductors which exhibited different physical properties from FeSC, or exploit new functionality of tetrahedral compounds. We focused on the mixed-anion compounds with layered structure which are the common characteristics with FeSC. After trial and error, we successfully synthesized new Fe and Co based mixed-anion compounds CaFeOS and CaCoOS. They bear the triangular lattice, and thus the exotic property derived from geometric frustration was expected. The transport property was non-metallic due to the relatively long distance of the Fe-Fe or Co-Co bonds. Although the superconductivity was not observed in the pristine sample, the specific heat measurement indicated that the orbital degeneracy existed in CaFeOS. We proposed that the geometric frustration induces the spin-orbital glassy state was realized in the system.

Alongside iron pnictides, manganese pnictides also attract much attention because of the strong electronic correlation. The ground state of AFM Mott insulator in manganese pnictide is reminiscent of the cuprate superconductor, where the high temperature superconductivity is induced from the insulating state by carrier doping. Moreover, the intriguing functionality such as the colossal magnetoresistance observed in $LaMnAsO_{1-x}H_x$ led us to the further materials exploration. We investigated the manganese-rich part of the ternary *A*(*AE*)-Mn-As systems, and discovered new manganese pnictides, (K, Rb, Cs)Mn_4As_3. In KMn_4As_3, $MnAs_4$ tetrahedra and $MnAs_5$ pyramids form the tunnel-type framework, while $RbMn_4As_3$ and $CsMn_4As_3$ adopt the double-layer-type structure composed of edge-sharing tetrahedra. They are Mott insulators with antiferromagnetic ordering. We discussed the structural relations in the *A*(*AE*)-Mn-As systems, and pointed out the structural similarity with *A*(*AE*)-Zn-As systems due to the stable d^5 and d^{10} electronic configuration. This relation of manganese and zinc pnictides is useful to design new functional materials such as magnetic

semiconductor. In addition, we attempted various kinds of impurity substitution on each compound. It is known that the carrier doping metallizes manganese pnictides although the superconductivity was not observed. However, the impurity substitution under ambient and high pressure condition was not achieved.

Accurate analysis of the magnetic property of double-layered (Cs, Rb)Mn_4As_3 was also performed using the powder neutron diffraction measurement. In the part of magnetism, it is known that the G-type AFM phase appears for BaMnAsF and $BaMn_2As_2$, while LaMnAsO exhibits the C-type AFM state where the intra-layer interaction is AFM and the inter-layer interaction is ferromagnetic. We found that (Cs, Rb)Mn_4As_3 are G-type antiferromagnets with the transition temperature at 480 K, which lies between that of $BaMn_2As_2$ (625 K) and LaMnAsO (380 K). The density functional theory calculation suggested that the electronic state of double-layered compound and single-layered compound is not largely different. However, the metallic and superconducting property in double-layered compounds remain attractive issues. We believe that the materials exploration to find double-layered FeSC such as $RbFe_4As_3$ and $CsFe_4As_3$ is strongly desirable.

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