論文の内容の要旨

Two-Dimensional Superconductivity in Layered R_2O_2Bi (*R*: Rare Earth) with Bi^{2-} Square Net

（Bi^{2-}正方格子を持つ層状化合物 R_2O_2Bi (*R*: 希土類)における 2 次元超伝導）

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1. Introduction

Bi square net compound is a promising platform to investigate the interaction between two-dimensional electronic nature and strong spin-orbit coupling. Layered $AMBi_2$ compounds (*A*: alkaline earth and rare earth, *M*: metal elements) with Bi^{-} square net have been extensively studied until today, leading to the emergence of the wide variety of quantum phenomena such as anisotropic Dirac fermion and Kondo lattice behavior, while superconducting Bi^{-} square net has not been realized yet. In contrast to the rich material group of Bi^{-} square net compounds, there are few reports about the synthesis of Bi^{2-} square net compounds except for $ThCr_2Si_2$-type R_2O_2Bi (*R*: rare earth) [1]. These compounds are considered as a counterpart of iso-structural Fe-based high temperature superconductor $BaFe_2As_2$ with the inverted carrier conduction layers: Bi^{2-} square net in R_2O_2Bi and $(Fe_2As_2)^{2-}$ slab in $BaFe_2As_2$ (Fig. 1), although only metal-to-insulator transition and antiferromagnetic ordering of *R* cations were reported so far in addition to the absence of superconductivity [1,2]. Therefore, detailed physical properties of Bi^{2-} square net is not fully understood despite the possible emergence of various attractive properties.

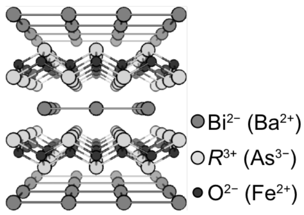

Figure 1. Crystal structure of R_2O_2Bi.

In this thesis, fascinating properties of Bi^{2-} square net in R_2O_2Bi compounds were explored via two approaches: the fabrication of epitaxial thin films and the synthesis of bulk polycrystalline powders. In thin film study, I succeeded in the fabrication of R_2O_2Bi epitaxial thin films for the first time by developing two novel solid-phase epitaxy techniques. Intrinsic two-dimensional electronic nature with strong spin-orbit coupling of Bi^{2-} square net was confirmed, and furthermore the onset of superconductivity was observed at low temperature. According to the results about epitaxial thin films, polycrystalline R_2O_2Bi samples were synthesized, connecting to the discovery of universal superconductivity of Bi^{2-} square net.

2. Development of solid-phase epitaxy techniques

Single crystalline samples were desired to investigate the intrinsic properties of R_2O_2Bi rather than polycrystalline powder specimen presently available. In this thesis, Y_2O_2Bi epitaxial thin films were successfully obtained by developing two solid-phase epitaxy techniques: reductive solid-phase epitaxy utilizing direct reaction between (Y,Bi) mixed powders and Y_2O_3 amorphous thin film, and multilayer solid-phase epitaxy utilizing subnanometer thick Bi/Y/Y_2O_3 multilayer precursor film. In both techniques, the reduction of Bi by strong reductant Y was essential to achieve Y_2O_2Bi phase. This concept would be applicable to the epitaxial growth of not only other R_2O_2Bi (e.g. R: Ce, Dy) compounds but also analogous layered compounds.

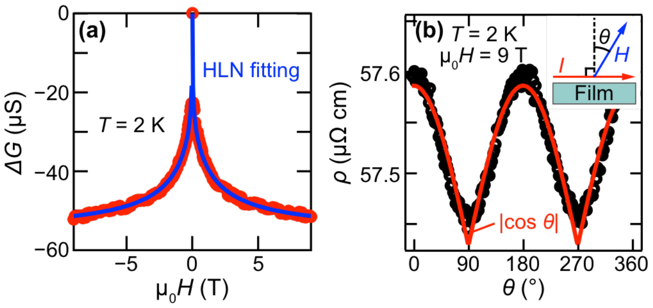

Figure 2. (a) Magnetoconductance at 2 K and (b) angular dependent magnetoresistance at 2 K and 9 T of Y_2O_2Bi epitaxial thin film. Inset of (b) denotes measurement configuration.

The detailed electrical transport properties were evaluated for Y_2O_2Bi epitaxial thin film. The film showed cusp-shaped magnetoconductance at 2 K with complete fitting by Hikami-Larkin-Nagaoka model, demonstrating weak anti-localization effect (Fig. 2a). In addition, two-fold symmetric angular dependent magnetoresistance was observed at 2 K and 9 T (Fig. 2b). These results indicated the interaction between two-dimensional electronic state and strong spin-orbit coupling in Bi^{2-} square net, similar to the topological insulator which is an innovative spintronic material. Furthermore, the onset of superconductivity was observed in several samples. However, both Meissner effect and zero resistance were not obtained probably due to very small superconducting volume fraction.

3. Two-dimensional superconductivity in polycrystalline R_2O_2Bi

In order to confirm the bulk nature of the superconductivity, polycrystalline Y_2O_2Bi samples were synthesized by varying the nominal amount of O in starting materials. As a result, abrupt c-axis expansion was observed only for the samples with high O content in contrast with constant a-axis length among all samples. This result suggested O incorporation between Bi^{2-} square net and adjacent Y termination layer in c-axis expanded samples (inset of Fig. 4). Figure 3 shows temperature dependence of magnetic susceptibility and electrical resistivity of Y_2O_2Bi samples. Both Meissner effect and zero-resistance were observed only for the samples with high O content, indicating bulk superconductivity. Superconducting transition temperature T_c was a monotonically increasing function of nominal amount of O. Furthermore, this new superconductor showed Berezinskii-Kosterlitz-Thouless transition, confirming two-dimensional superconductivity of Bi^{2-} square net in Y_2O_2Bi. This was the first observation of superconducting Bi square net.

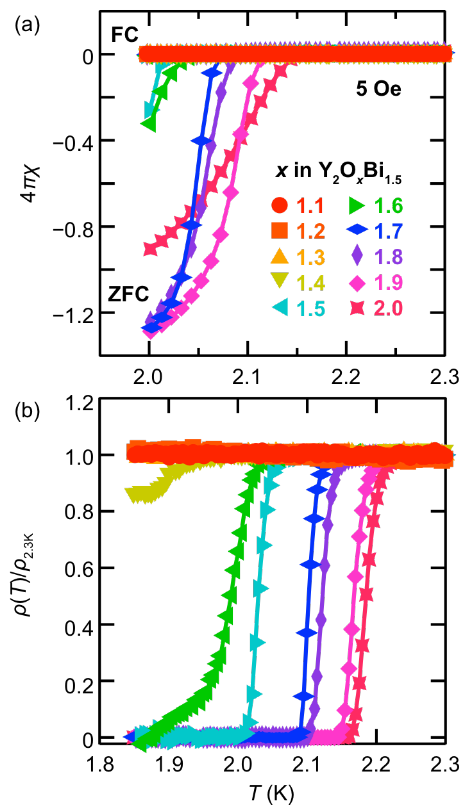

Figure 3. Temperature dependence of (a) magnetic susceptibility and (b) normalized electrical resistivity of Y_2O_2Bi samples with different nominal amount of O, x.

Figure 4 shows T_c plot as a function of Bi inter-net distance d ($d = c/2$). The superconductivity emerged concomitantly with the abrupt expansion of d, and T_c was monotonically increasing function of d. This result indicates that the superconductivity in Y_2O_2Bi was induced by enhancing two-dimensionality of Bi^{2-} square net. Such nonstoichiometric atom incorporation into hidden interstitial site could be a new methodology to induce superconductivity in layered compounds.

Furthermore, the superconductivity was also observed in other R_2O_2Bi (R: Tb, Dy, and Lu) by same driving force: enhanced two-dimensionality of Bi^{2-} square net via O incorporation was crucial to induce the superconductivity. Notably, complex phase competition among the superconductivity, antiferromagnetic ordering, and charge density wave was observed in Tb_2O_2Bi, indicating unusual mechanism of the superconductivity in Bi^{2-} square net. The universal superconductivity with rich electronic phases depending on R in R_2O_2Bi indicated that R_2O_2Bi would provide intriguing platform to investigate the interplay between two-dimensional superconductivity and strong spin-orbit coupling.

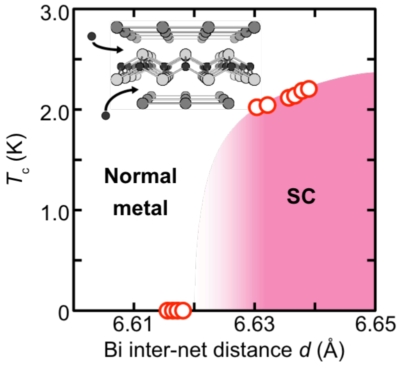

Figure 4. Superconducting phase diagram of Y_2O_2Bi as a function of d. Inset shows schematic image of O incorporation. SC: superconducting.

4. Conclusion

In conclusion, I established the novel routes to investigate the physical properties of Bi^{2-} square net in R_2O_2Bi compounds. According to these techniques, I clarified the rich electronic phenomena of Bi^{2-} square net such as universal two-dimensional superconductivity and similar electronic nature to the topological insulator. These findings indicate that R_2O_2Bi was the model compound to investigate the peculiar phenomena of Bi^{2-} square net. Furthermore, obtained concepts such as two solid-phase epitaxy techniques and the emergence of superconductivity by structural control via O incorporation would provide the insight for exploring physical properties of layered compounds.

References

[1] H. Mizoguchi *et al.*, *J. Am. Chem. Soc.* **133**, 2394 (2011).

[2] H. Hosono *et al.*, *Sci. Technol. Adv. Mater.* **16**, 033503 (2015).