Superconductivity in BiS$_2$-Based Layered Compounds

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Abstract

Crystal structure and physical properties of the novel BiS$_2$-based layered superconductors are briefly reviewed. Superconductivity in the BiS$_2$-based layered compounds is induced by electron doping into the BiS$_2$ conduction layers. The superconducting properties seem to correlate with the crystal structure. Possible strategies for increasing transition temperature in this family are discussed.

Keywords: Layered superconductor; BiS$_2$-based superconductor; Crystal structure; Physical property

1. Introduction

Since the discovery of the cuprate layered superconductors, materials possessing a layered crystal structure have been one of the mostly-studied systems on exploration of new superconductors [1]. The discovery of the Fe-based superconductors in 2008 has also accelerated studies on new layered materials [2]. One of the reasons for the tremendous amount of attentions in the layered superconductors is the observation of unconventional paring mechanisms due to low-dimensional characteristics of conductive electrons. Another merit of layered materials in exploring for new superconductors is the variation of crystal structure. In general, the layered superconductors possess a crystal structure composed of an alternate stacking of a common superconducting layer and a blocking (spacer) layer. In the Fe-based family, the Fe$_2$An$_2$ layers (An = P, As, S, Se or Te) could act as a common superconducting layer, and a lot of Fe-based superconductors have been discovered by changing the blocking layer structure [2-4]. Namely, if we discover a new type of superconducting layers, we can design a lot of layered...
superconductors. In 2012, the novel layered superconductors with a BiS$_2$-based superconducting layer have been discovered [5,6]. So far, 11 superconductors have been discovered, and some notable characteristics have been observed in this family [7-11]. Here, the crystal structure and physical properties of the BiS$_2$-based superconductors are briefly reviewed.

2. Crystal structure and superconducting properties

Figure 1(a) and (b) show the schematic images of the crystal structure of typical BiS$_2$-based superconductor LaOBiS$_2$ and Bi$_4$O$_4$S$_3$, respectively. Both materials are composed of an alternate stacking of the BiS$_2$ double layers and the blocking layer. Electron carriers, which are essential for the appearance of superconductivity in the BiS$_2$-based family, can be generated (controlled) by modifying the structure and the composition at the blocking layers. In the REOBiS$_2$ system (RE = Rare earth), electron carriers can be generated upon a partial substitution of O$^2-$ by F$^-$ [6], which is an electron-doping strategy used in the FeAs-based superconductors. In the Bi$_4$O$_4$S$_3$ superconductor, partial defects at the (SO$_4$)$_2^-$ site can provide electron carriers into the BiS$_2$ layers [5].

Fig. 1. (a) Crystal structure of LaOBiS$_2$. (b) Crystal structure of Bi$_4$O$_4$S$_3$. In this figure, the structure is depicted with full site occupancy: Namely, the elemental composition of the shown structure is Bi$_6$O$_8$S$_5$. In real, there would be ~50% defects at the (SO$_4$)$_2^-$ site, which corresponds to the composition of Bi$_4$O$_4$S$_3$.

The physical properties of BiS$_2$-based compounds are introduced with the data of the LaO$_{1-x}$F$_x$BiS$_2$ system. Figure 2(a) displays the temperature dependence of resistivity for LaOBiS$_2$ (parent phase) and LaO$_{0.5}$F$_{0.5}$BiS$_2$. The parent phase exhibits semiconducting transport behavior. With the partial substitution of O by F, the resistivity decreases and superconducting transition is observed at ~3 K for LaO$_{0.5}$F$_{0.5}$BiS$_2$. The superconducting properties can be enhanced by annealing the LaO$_{0.5}$F$_{0.5}$BiS$_2$ superconducting sample under high pressure (HP). Figure 2(b) shows the temperature dependence of resistivity for as-grown and HP-annealed LaO$_{0.5}$F$_{0.5}$BiS$_2$. The onset of the transition temperature ($T_c$) is clearly enhanced from 3 to 10.6 K by the HP annealing [6,10]. It was found that the uniaxial strain (contraction) along the c axis is generated by the HP annealing [11]. These facts indicate that the optimization local structure is essential for the appearance of bulk superconductivity at a higher temperature in the BiS$_2$-based superconductors. It was also reported that the application of external pressure could enhance the $T_c$ of as-grown LaO$_{0.5}$F$_{0.5}$BiS$_2$. Furthermore, the crystal structure analysis under HP showed that the structural transition from tetragonal to monoclinic was positively linked with the enhancement of $T_c$ under high pressure [12]. Theoretical investigations suggested that the slight changes in the local crystal structure such as the z coordinate of S at the BiS$_2$ layer could largely affect the band structure [13,14]. In these regards, the correlation between superconductivity and
local crystal structure should be important to understand the mechanisms and to enhance the $T_c$ in the BiS$_2$-based superconductors.

Figure 3(a) shows the temperature dependence of normalized resistivity around superconducting transition for the typical BiS$_2$-based superconductors, LaO$_{0.5}$F$_{0.5}$BiS$_2$ (HP-annealed), CeO$_{0.3}$F$_{0.7}$BiS$_2$ (HP-annealed), NdO$_{0.7}$F$_{0.3}$BiS$_2$ (as-grown) and Bi$_4$O$_4$S$_3$ (as-grown). Here the transport data for the samples with the highest $T_c$ in the respective systems are summarized. The midpoints of $T_c$ are summarized in Fig. 3(b). To discuss the tendency of the $T_c$, the area where the superconducting properties ($T_c$) are optimized is highlighted with a green square. The optimized $T_c$ in the LaOBiS$_2$ system is the highest. Then, the optimized $T_c$ tends to decrease by changing the blocking layer structure in an order of La$_2$O$_3$, Ce$_2$O$_3$, Nd$_2$O$_3$ and Bi$_4$O$_4$(SO$_4$). The tendency can be understood with the change in the ionic radius of the anion (La$^{3+}$, Ce$^{3+}$, Nd$^{3+}$ and Bi$^{3+}$) in the blocking layer. The ionic radius of the anion directly tune the $a$ axis length in this family. In fact, the optimized $T_c$ in the BiS$_2$-based superconductors well correlates with the length of the $a$ axis.

Fig. 2. (a) Temperature dependence of resistivity for LaOBiS$_2$ and LaO$_{0.5}$F$_{0.5}$BiS$_2$. (b) Temperature dependence of resistivity for as-grown and HP-annealed LaO$_{0.5}$F$_{0.5}$BiS$_2$.

Fig. 3. (a) Temperature dependence of normalized resistivity around superconducting transition for the typical BiS$_2$-based superconductors, LaO$_{0.5}$F$_{0.5}$BiS$_2$ (HP-annealed), CeO$_{0.3}$F$_{0.7}$BiS$_2$ (HP-annealed), NdO$_{0.7}$F$_{0.3}$BiS$_2$ (as-grown) and Bi$_4$O$_4$S$_3$ (as-grown). (b) Transition temperatures (midpoint) are summarized.
3. Strategies to enhance superconducting properties

In the above, possible two structural parameters are suggested to be essential for superconductivity in the BiS$_2$ family. The first one is the local structure correlated with the uniaxial compression along the $a$ axis, which can be optimized by applying high pressure. This should be essential for the appearance of bulk superconductivity in the respective systems. The other parameter is the length of the $a$ axis, which can be tuned by changing the blocking layer. Unfortunately, the largest rare earth is La; hence, we cannot synthesize new REOBiS$_2$ materials with larger $a$ axis. Therefore, we should discover new blocking layers. For example, the structure similar to Bi$_6$O$_3$S$_3$, Fig. 1(b), is a candidate. If the Bi could be substituted with rare earth, larger $a$ axis could be obtained. Another strategy is to use a perovskite-oxide blocking layer, which is formed in the Fe-based superconductor Sr$_2$Sc$_2$O$_6$Fe$_2$P$_2$ [17].

Recently, superconductors with Bi-Se and Bi-Te conduction layers were discovered. Maziopa et al. reported that LaO$_{0.8}$F$_{0.2}$BiSe$_2$ with a structure similar to LaOBiS$_2$ showed superconductivity below 2.6 K [18]. Malliakas et al. reported that CsBi$_5$Te$_6$ exhibited superconductivity below 4.4 K by hole-carrier doping [19]. The Bi-Te blocks of CsBi$_5$Te$_6$ are similar to the NaCl structure as well as the BiS$_2$ layers. Therefore, superconductivity observed in doped CsBi$_5$Te$_6$ could be driven with the mechanisms same as the BiS$_2$-based superconductors. Hence, replacement of BiS$_2$ layers by Bi-Se or Bi-Te layers could be a promising strategy for enhancing $T_c$ of Bi-based superconductors.

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References

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