Pb Substitution effect in La(O,F)BiSSe

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BiS₂-based superconductors \( \text{Ln}(O,F)\text{BiCh}_2 \) (\( \text{Ln} = \text{La, Ce, Nd...} \), \( \text{Ch} = \text{S, Se} \)) have layered structure and these superconducting critical temperatures (\( T_c \)) change by doping carriers or applying chemical pressure by element substitution. For example, it is reported that the \( T_c \) were enhanced by Pb substitution in \( \text{Nd}(O,F)\text{BiS}_2 \)\(^{[1]}\). Moreover, anomalous behaviors in temperature dependence of electrical resistivity were observed in Pb substituted \( \text{La}(O,F)\text{BiS}_2 \) single crystals\(^{[2]}\). It is interesting problem whether such Pb substitution effects occur in other BiS₂-based materials. To verify this, we investigated Pb substitution effects in \( \text{La}(O,F)\text{Bi}_{1-x}\text{Pb}_x\text{S}_2 \) (\( x = 0, 0.02, 0.04, 0.08 \)) single crystals because \( \text{La}(O,F)\text{BiSSe} \) has the highest \( T_c \) in \( \text{La}(O,F)\text{BiCh}_2 \) in ambient pressure\(^{[3]}\).

From X-ray diffraction experiment, decrease of a-axis length was observed with increasing Pb concentration indicating successful Pb substitution. In contrast to the results in \( \text{La}(O,F)\text{BiS}_2 \), \( T_c \) decreases with increasing Pb concentration in both magnetization and electrical resistivity measurements. Furthermore, the anomalous behavior which has observed for \( \text{La}(O,F)\text{Bi}_{1-x}\text{Pb}_x\text{S}_2 \) in resistivity measurement was not observed in all Pb concentrations.

\(^{[1]}\) S. Demura et al., Solid State Communications 223 (2015) 40-44
\(^{[2]}\) S. Demura (in preparation)

Keywords: BiS₂-based superconductor, in-plane chemical pressure
Unidirectional pressure effect on electrical resistivity in single crystal La(O,F)BiS$_2$

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LaOBiS$_2$ has a crystal structure composed of an alternate stacking of conducting layers (BiS$_2$ layers) and spacer layers (LaO layers). Carrier doping by partial substitution of F for O induces superconductivity with a transition temperature ($T_c$) of 3K [1]. According to preceding study, $T_c$ in La(O,F)BiS$_2$ was enhanced by application of hydrostatic pressure[2]. $T_c$ was also increased by partial substitution of S$^2$ by Se$^2$, which induces in-plane pressure [3]. These reports indicate that $T_c$ in La(O,F)BiS$_2$ is thought to be sensitive to structural perturbations, especially in-plane structural perturbation. The in-plane structural instability was also predicted theoretically.

We have tried to measure electric properties in La(O,F)BiS$_2$ under in-plane structural perturbation. We performed electrical resistivity measurements under application of uniaxial stress using a piezo actuator, which can expand the sample unidirectionally by application of voltage. We have succeeded to measure electrical resistance under the unidirectional stress at room temperature, liquid nitrogen temperature and liquid helium temperature. At the conference, we will discuss the results.


Keywords: BiS$_2$ based superconductor, in-plane chemical pressure
F Substitution Effect on supermodulation in LaO$_{1-x}$F$_x$BiSe$_2$ Studied by STM

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In BiS$_2$ based superconductors such as LaO$_{1-x}$F$_x$BiCh$_2$ (Ch = S, Se), the electronic properties are controlled by the carrier density, which is determined by the amount of substituted F. Above $x=0.5$, this material is predicted theoretically to exhibit charge density wave instability which shows supermodulation on BiS$_2$ plane due to the phonon instability and the fermi surface nesting [1]. Recently, in LaO$_{0.5}$F$_{0.5}$BiSe$_2$ single crystals, scanning tunnelling microscopy and spectroscopy (STM/STS) measurements revealed the appearance of supermodulation on BiSe$_2$ plane [2], whose period is different from that predicted from the Fermi surface nesting. To certify whether this observed modulation is one due to the Fermi surface nesting or not, we performed STM/STS experiments on samples with different F concentrations. STM/STS measurements were performed on $x = 0.1$ and $x = 0.5$ samples at 4.2 K. The observed surface was prepared by cleavage at 4.2 K in situ.

STM/STS observations revealed that the supermodulation existed in both $x = 0.1$ and $x = 0.5$ samples. Furthermore, the period of the modulation was five times of the lattice constant regardless of the carrier concentration. This indicates that the observed modulation is not caused by the electronic origin such as the Fermi surface nesting.


Keywords: BiS$_2$, BiSe$_2$
Scanning tunneling microscopic observation in LaO$_{1-x}$F$_x$Bi$_{1-y}$Pb$_y$S$_2$

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BiS$_2$-based superconductors $Ln$(O,F)Bi$Ch_2$ ($Ln$=La,Ce,Nd... , $Ch$=S,Se) have a layered crystal structure which resembles that of copper oxide superconductors. In addition, their properties are changed by career doping or elemental substitution. In LaO$_{0.5}$F$_{0.5}$BiS$_2$, we discovered that the superconducting properties are enhanced by partial substitution of Pb for Bi. In addition, it was found that the temperature dependence of resistivity in LaO$_{1-x}$F$_x$Bi$_{1-y}$Pb$_y$S$_2$ shows anomalous behavior. To investigate the effect of Pb substitution microscopically, we performed STM/STS measurements in LaO$_{0.5}$F$_{0.5}$BiS$_2$ and LaO$_{0.5}$F$_{0.5}$Bi$_{0.92}$Pb$_{0.08}$S$_2$. The single crystals used in this study were synthesized by the CsCl/KCl flux method.

A square lattice of Bi atoms was observed on the cleaved surface of LaO$_{0.5}$F$_{0.5}$Bi$_{0.92}$Pb$_{0.08}$S$_2$. However, the observed surface was rather rough in contrast to the flat surface observed in other BiS$_2$-based superconductors. In addition, tunneling spectra changed locally. These features are considered as the characteristics of Pb substituted system. In parent material (LaO$_{0.5}$F$_{0.5}$BiS$_2$), we have not obtained a clear STM image so far. This seems to indicate low density of states at $E_F$ in LaO$_{0.5}$F$_{0.5}$BiS$_2$.

Keywords: p-electron system, tunneling microscopy, substitution effect
Observation of Superconducting gap and Vortex lattice in the transition metal tri-calchogenide ZrTe$_3$-$x$Se$_x$ by Scanning Tunneling Spectroscopy

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Transition metal tri-calchogenide ZrTe$_3$ has the quasi one dimensional layered system: a layer formed by trigonal prismatic ZrTe$_6$ chains elongated along the $b$ axis is stacked along the $c$ axis. Because of the crystal structure, this material shows an anisotropic resistivity in the in-plane and along the $c$ axis direction. Furthermore, this material shows a charge density wave at around 63 K along the $a$ axis and filamentary superconductivity below 2 K. Recently, it is reported that the bulk superconductivity appears at around 4 K by the Se substitution of 4 % for Te [1]. Therefore, the anisotropic superconducting properties due to the anisotropic crystal structure are expected.

In this study, an observation of superconducting gap and vortex lattice was performed in ZrTe$_{1-x}$Se$_x$ using a scanning tunnelling microscopy and spectroscopy (STS) measurement at 2 K to investigate the anisotropic superconducting properties. From the STS measurement, the superconducting gap and the anisotropic vortex lattice were successfully observed on the surface of ZrTe$_{1-x}$Se$_x$. We will report these results in detail in the presentation.


Keywords: Superconductivity, vortex, STM/STS
Crystal structure and physical properties of layered compound LaOSbSe$_2$

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We report on the crystal structure and physical properties of a novel layered compound LaOSbSe$_2$. The compound crystallizes in a tetragonal structure with space group $P4/nmm$. The structure consists of alternately stacked layers of LaO and bilayers of SbSe$_2$, and is isostructural with BiS$_2$-based superconductors such as LaO$_{1-x}$F$_x$BiS$_2$. Electric resistivity measurements revealed that LaOSbSe$_2$ is a semiconductor. We will also report on the effects of chemical doping, as well as first-principles calculations.

Keywords: BiS$_2$ superconductors, chemical substitution, new materials, SbSe$_2$ layers
Crystal Growth and Superconducting Properties of Topological Superconductor Candidates $A_x$Bi$_2$Se$_3$ ($A = \text{Sr, Nb}$)

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Bi$_2$Se$_3$ is well known as a typical topological insulator. After the discovery of superconductivity in Cu-intercalated Bi$_2$Se$_3$ (Cu$_x$Bi$_2$Se$_3$) [1], it became a promising topological superconductor candidate. The topological superconductor is theoretically predicted to have topologically nontrivial surface/edge states, which can host Majorana fermions. These fermions follow non-Abelian statistics and are expected to be applied to quantum computers. However, Cu$_x$Bi$_2$Se$_3$ has several problems such as inhomogeneity, unstable in the air, low superconducting volume fractions. Recently, it was reported that Sr and Nb intercalated Bi$_2$Se$_3$ (Sr$_x$Bi$_2$Se$_3$, Nb$_x$Bi$_2$Se$_3$) also showed superconductivity [2, 3].

In this study, we have grown single crystals of Sr$_x$Bi$_2$Se$_3$ by the melt growth method. Large single crystals have been successfully obtained. In contrast to Cu$_x$Bi$_2$Se$_3$, the shiny metallic surface of Sr$_x$Bi$_2$Se$_3$ remains even after exposure to the air for a long time. From transport measurements, superconductivity was confirmed in Sr$_x$Bi$_2$Se$_3$ single crystals. The transition temperature monotonically increased with nominal compositions, up to ~ 3.2 K for $x = 0.25$. The resistivity under various magnetic fields was also measured and the superconducting parameters were determined using the WHH and GL models. We will also discuss crystal growth and transport properties in single crystals of Nb$_x$Bi$_2$Se$_3$, including a comparison of $A_x$Bi$_2$Se$_3$ ($A = \text{Cu, Sr, Nb}$).


Keywords: Topological superconductor, Crystal growth, Superconducting parameters
Crystal Growth and Superconducting Properties of Pb-doped NiBi$_3$ having Strong Spin-Orbit Coupling

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Topological electric phases are expected to appear in materials composed of heavy elements due to the band inversion by strong spin-orbit coupling. In case of a topological superconductor, while a superconducting gap exists in the bulk, unique gapless states hosting Majorana fermions are predicted to emerge in the surface or at the edge and inside the magnetic flux core. In this study, as a candidate of a topological superconductor, we have investigated NiBi$_3$ ($T_c = 4.06$ K [1]), which is expected to have strong spin-orbit coupling due to bismuth. NiBi$_3$ has a crystal structure composed of one-dimensional atomic chains, which are bonded in two perpendicular directions by van der Waals force. We have considered NiBi$_3$ is an excellent material for the exploration of topological superconducting materials because it has relatively high $T_c$, the stoichiometric composition, and is stable in the atmosphere.

From the results of the first principles calculations, it was confirmed that electronic structures in NiBi$_3$ were significantly influenced by spin-orbit coupling. Furthermore, theoretical calculations suggested that hole-carrier doping could increase $T_c$. Therefore, we have tried to substitute Pb for Bi to dope hole carries. We succeeded in growing single crystals of NiBi$_{3-x}$Pb$_x$ with $x = 0.0$ to $0.3$ by using the self-flux method. The temperature and the magnetic-field dependences of the resistivity in NiBi$_{3-x}$Pb$_x$ crystals were measured, respectively. In accord with the theoretical prediction, $T_c$ slightly increases with the amount of Pb doping ($x$). As compared with the slight enhancement of $T_c$, it was found that the critical field remarkably increased: about three times higher in NiBi$_{2.7}$Pb$_{0.3}$ than that of pure NiBi$_3$.


Keywords: NiBi$_3$, Superconducting Properties, Single Crystal, Electronic Structures
Effect of Sulfur and Selenium Substitution on ZrTe$_3$

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ZrTe$_3$ is one of transition metal trichalcogenide compounds, having the structure composed of triangular prismatic chains. This material undergoes a charge density wave (CDW) transition at 63 K and shows filamentary superconductivity below 2 K. Recent paper reported that partial Se substitution with Te of 4% suppressed the CDW order and induced bulk superconductivity at around 4 K [1]. Since the ionic radius of Se is smaller than that of Te, superconductivity is possibly induced through lattice strain caused by the element substitution. Therefore, substitution of S ion, which has the smaller ionic radius than that of Se ion, is promising way to increase superconducting transition temperature ($T_c$).

In this study, we synthesized ZrTe$_{3-x}$Ch$_x$ ($Ch = S, Se$) single crystals and measured their superconducting properties. The sample substituted for S ion of 10% shows superconductivity at 3 K in a magnetic susceptibility measurement. At the conference, we will discuss the difference in superconducting properties between S and Se substituted samples.


Keywords: charge density wave, trichalcogenide