

学位論文の要旨

Abstract of Thesis

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学位論文題目 Title of Thesis (学位論文題目が英語の場合は和訳を付記)

Syntheses and characterisations of new metal-doped iron chalcogenide superconductors
 新規な金属ドーピング鉄カルコゲナイド超伝導体の合成と評価

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A search for new superconductors exhibiting high superconducting transition temperatures (T_c 's) is one of the most exciting and significant researches. During past 100 years, many superconductors have been reported and the highest T_c reaches 166 K (fluorinated $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ at 23 GPa [1]); very recently, 203 K superconductivity of H_2S was discovered [2]. Currently, iron based superconductors, iron pnictide and iron chalcogenide, attract much attention because of the discovery of a wide variety of materials exhibiting high T_c 's.

The iron chalcogenide, $\beta\text{-FeSe}$, showed the T_c as high as 8.5 K [3] which has the PbO-type simple structure (called as '11' type). In 2010, the metal doping of $\beta\text{-FeSe}$ with K atom led to the rapid increase in T_c from 8.5 to 31 K [4]. The subsequent study on metal doping using liquid NH_3 technique resulted in the higher T_c in metal doped FeSe. The highest T_c is currently 46 K for $(\text{NH}_3)_y\text{Na}_x\text{FeSe}$ at ambient pressure. Thus, 'intercalation chemistry' can make a strong contribution in synthesising new superconductors of iron chalcogenides.

In this Doctor thesis, the author reported on superconductivity of metal doped $\text{FeSe}_{1-z}\text{Te}_z$ ($0 \leq z \leq 1$), $(\text{NH}_3)_y\text{M}_x\text{FeSe}_{1-z}\text{Te}_z$, synthesised using liquid NH_3 technique. The first purpose of this study is to clarify systematically the chemical and physical properties of $(\text{NH}_3)_y\text{M}_x\text{FeSe}$. For this purpose, various $(\text{NH}_3)_y\text{M}_x\text{FeSe}$ materials were synthesised using the liquid NH_3 technique, and their magnetic and transport properties were investigated in wide pressure and temperature ranges. The structures of $(\text{NH}_3)_y\text{M}_x\text{FeSe}$ materials prepared in this study were determined using Le Bail fitting and Rietveld refinement for X-ray diffraction (XRD) patterns. The second purpose is to determine the parameters dominating the T_c in $(\text{NH}_3)_y\text{M}_x\text{FeSe}$. Throughout this study, it was found that the T_c was scaled with the FeSe plane spacing (or

lattice constant, c), and the FeSe plane spacing was closely associated with the location of metal atoms. The third purpose of this study is to determine the exact structure of metal doped FeSe. She successfully determined the crystal structure of $(\text{NH}_3)_y\text{Cs}_{0.4}\text{FeSe}$ based on the Rietveld refinement for XRD pattern at low temperature. Furthermore, she reported the behaviour of T_c of $(\text{NH}_3)_y\text{M}_x\text{FeSe}$ under high pressure and the isotope effect of T_c in $(\text{ND}_3)_y\text{M}_x\text{FeSe}$'s which were prepared with liquid ND_3 .

In chapter 4, the author described syntheses and characterisations of the alkali-metal doped FeSe, $(\text{NH}_3)_y\text{M}_{0.4}\text{FeSe}$ (M: K, Rb and Cs), prepared using liquid NH_3 technique. The new superconducting materials, $(\text{NH}_3)_y\text{Cs}_{0.4}\text{FeSe}$, showed the T_c as high as 31.2 K, which is higher by 3.8 K than the T_c of non-ammoniated $\text{Cs}_{0.4}\text{FeSe}$. The $(\text{NH}_3)_y\text{K}_{0.4}\text{FeSe}$ and $(\text{NH}_3)_y\text{Rb}_{0.4}\text{FeSe}$ materials were also synthesised. From the $T_c - c$ plot prepared based on the data collected from her study and other references [5,6], the correlation between the T_c and FeSe plane spacing was clarified, suggesting that an increase in Fermi-surface nesting produced the higher T_c .

In chapter 5, the author described the presence of multiple superconducting phases (low- T_c and high- T_c) in $(\text{NH}_3)_y\text{Na}_x\text{FeSe}$. The T_c of $(\text{NH}_3)_y\text{Na}_x\text{FeSe}$ was investigated as a function of x . The low- T_c phase ($T_c = 32$ K) was found in the low- x range below 0.4, while the high- T_c phase ($T_c = 45$ K) was observed in the high- x range, showing that the T_c depends significantly on x . The T_c changed discontinuously from 32 to 45 K.

The crystal structure (space group) of $(\text{NH}_3)_y\text{Na}_x\text{FeSe}$ did not change with increasing x up to 1.1, *i.e.*, all $(\text{NH}_3)_y\text{Na}_x\text{FeSe}$'s ($x = 0.1$ to 1.1) possessed the space group of $I4/mmm$. The lattice constants, a and c , for the low- T_c phase ($T_c = 32.5$ K) were 3.9120(9) and 14.145(8) Å, respectively, while $a = 3.8266(7)$ Å and $c = 17.565(9)$ Å for the high- T_c phase (~ 46 K). The c for the high- T_c phase is larger than that of the low- T_c phase, implying that the T_c is directly related to the c . The author suggested that the sites occupied by metal atoms differed from each other between two phases. Namely, the position of Na atom in $(\text{NH}_3)_y\text{Na}_x\text{FeSe}$ may change from on-centre ($2a$ site) to off-centre sites ($4c$ and $2b$ sites) with increasing x . Depending on the variation of location of metal atom, the low- T_c phase may change to the high- T_c phase.

Contrary to $(\text{NH}_3)_y\text{Na}_x\text{FeSe}$, the $T_c - x$ plot showed a dome-like (continuous) behaviour in $(\text{NH}_3)_y\text{Li}_x\text{FeSe}$, suggesting that the Li atom in $(\text{NH}_3)_y\text{Li}_x\text{FeSe}$ occupies the off-centre sites ($4c$ and $2b$ sites) over the entire x -range, 0.1 – 1.0. The T_c was constant within ± 2 K in $(\text{NH}_3)_y\text{Cs}_x\text{FeSe}$ when varied x from 0.03 to 1.3, suggesting that the Cs atom occupied the $2a$ site (on-centre structure) in all x range of 0.03 to 1.3.

In chapter 6, the author performed the structural analysis by means of the Rietveld refinement for the XRD pattern of $(\text{NH}_3)_y\text{Cs}_{0.4}\text{FeSe}$ at 30 K. In the Rietveld analysis, two different structure models, on-centre and

off-centre, were examined under the space group of $I4/mmm$. This analysis finally showed that the Cs occupied the $2a$ site and the N of NH_3 occupied the $4c$ site, *i.e.*, on-centre structure. The result supports the scenario that the low- T_c phase changes to the high- T_c phase through the variation of location of Na atom, as described in chapter 5.

In chapter 7, the author reported the pressure dependence of superconductivity of the high- T_c and low- T_c phases of $(\text{NH}_3)_y\text{Na}_x\text{FeSe}$, and $(\text{NH}_3)_y\text{Li}_x\text{FeSe}$, which was investigated using DC magnetic susceptibility in a pressure range of 0 – 1 GPa. The T_c decreased monotonously with an increase in pressure up to near 1.0 GPa. The temperature dependence of resistance is also reported for $(\text{NH}_3)_y\text{Li}_x\text{FeSe}$. To investigate the isotope effect of T_c , the metal doped FeSe samples were synthesised using liquid ND_3 instead of NH_3 , and the superconductivity of $(\text{ND}_3)_y\text{M}_x\text{FeSe}$ (M: Na and Cs) was consistent with that of $(\text{NH}_3)_y\text{M}_x\text{FeSe}$ (M: Na and Cs), implying that NH_3 does not play an important role in superconductivity.

In chapter 8, the high- T_c phase, $(\text{NH}_3)_y\text{Na}_{0.5}\text{FeSe}_{0.5}\text{Te}_{0.5}$, showing the T_c of 27 K was fully investigated. The NH_3 amount was determined to be in 0.6 – 0.7. The high- T_c phase would be a metastable phase because of the rapid conversion from the high- T_c ($T_c = 27$ K) to the low- T_c ($T_c = 20$ K) phase within three days. The comparison of structure and physical properties between these phases is briefly described.

This Doctor thesis reports the systematic study on metal doped FeSe synthesised by using the liquid NH_3 technique. The superconductivity and structures were clarified for various $(\text{NH}_3)_y\text{M}_x\text{FeSe}$ materials. In particular, the discovery of the relationship between the T_c and c (or FeSe plane spacing), the finding of multiple superconducting phases and the clarification of origin of two phases are of significance for the advancement of research on FeSe based superconductors. Furthermore, the syntheses of metal doped FeSe using liquid ND_3 and the research of metal doped $\text{FeSe}_{0.5}\text{Te}_{0.5}$ are also of significance for the development of high- T_c metal doped chalcogenide superconductors. Part of this Doctor thesis has already been published in refs. 6 and 7, and one paper was submitted to a physics journal.

References:

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