Unconventional isotope effect on transition temperature in BiS₂-based superconductor Bi₄O₄S₃

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Abstract

We report the sulfur isotope effect on transition temperature in a BiS₂-based superconductor Bi₄O₄S₃. Polycrystalline samples of Bi₄O₄S₃ were prepared using ^{32}S and ^{34}S isotope chemicals. From magnetization analyses, the isotope exponent (α_S) was estimated as $-0.1 < \alpha_S < 0.1$. Although the T_c estimated from electrical resistivity was scattered as compared to those estimated from the magnetization, we observed no clear correlation between T_c and the isotope mass. The present results suggest that unconventional paring states are essential in Bi₄O₄S₃.

1. Introduction

Superconducting pairing mechanisms in most superconductors are achieved by electron-phonon interactions and explained by the Bardeen–Cooper–Schrieffer (BCS) theory [1]. However, there are unconventional superconductors whose pairing is not mediated by phonon. The typical examples of unconventional superconductors are the layered cuprate and Fe-based high-transition-temperature (high-T_c) superconductors [2,3], in which pairing is mediated by spin and/or orbital fluctuations [4,5]. Although there are various ways to test if the superconductivity mechanisms are mediated by phonon or other fluctuations, studying isotope effect on T_c is a direct probe to examine the importance of phonon to the superconductivity. Based on the conventional phonon-mediated model, T_c should be proportional to its phonon energy $\hbar\omega$, where $\hbar$ and ω are the Planck constant and phonon frequency, respectively. The T_c of a conventional superconductor is, therefore, sensitive to the isotope effect of the constituent elements. The isotope exponent α, which is defined by $T_c \sim M^{-\alpha}$, where M is the isotope mass, is expected to be $\alpha \sim 0.5$ from the conventional model [1]. For example, α close to 0.5 has been reported for a bismuth oxide $(Ba,K)BiO_3$ ($\alpha_O \sim 0.5$) [6], doped fullerene ($\alpha_C \sim 0.4$) [7], MgB_2 ($\alpha_B \sim 0.3$) [8], and borocarbides ($\alpha_B \sim 0.3$) [9]. In contrast, α different from 0.5 has been reported for unconventional superconductors. In the cuprate superconductor system, α_O deviates from 0.5 and exhibits anomalous carrier concentration dependence [10,11]. In the Fe-based superconductor, an inverse isotope effect, negative α_{Fe}, for the same composition [12].

In this study, we focus on the BiS_2-based layered superconductors, which was discovered in 2012 [13-15]. Since the layered structure composed of alternate stacking of a conduction layer (BiS_2 layer) and an insulator layer is quite similar to that of the high-T_c superconductors, elucidation of the mechanisms of superconductivity in BiS_2-based superconductors has been desired; however, it is still controversial [16,17]. In the early stage, theoretical and experimental studies reported the possibility of conventional electron-phonon superconductivity in the BiS_2-based compounds [18-21]. However, some of theoretical studies suggested the possibility of unconventional mechanisms of superconductivity in the BiS_2-based system [22-24]. In addition, the possibility of unconventional mechanisms was experimentally suggested from angle-resolved photoemission spectroscopy in $NdO_{0.71}F_{0.29}BiS_2$ [25] and the Se-isotope effect in $LaO_{0.6}F_{0.4}BiSSe$ ($-0.04 < \alpha_{Se} < 0.04$) [26]. Therefore, further experimental investigations on the mechanisms are desired for the BiS_2-based superconductor family. To investigate the S isotope effect on T_c, we selected $Bi_4O_4S_3$ to be a target phase of this study because its T_c is relatively high ($T_c > 4.5$ K), the transition is relatively sharp, and the composition is the simplest (ternary) among the BiS_2-based superconductors [13, 27-29]. Here, we show that the $Bi_4O_4S_3$ superconductor samples prepared with ^{32}S and ^{34}S isotope chemicals did not show conventional-type isotope effect on T_c, and the estimated α_S was close to zero. This result proposes

that the unconventional isotope effect is universal feature between $LaO_{0.6}F_{0.4}BiSSe$ with a BiSSe-type superconducting layer and $Bi_4O_4S_3$ with a BiS_2-type superconducting layer.

2. Experimental details

Polycrystalline samples of $Bi_4O_4S_3$ were prepared by a solid-state-reaction method. Powders of Bi (99.999%) and Bi_2O_3 (99.999%) were mixed with powders of ^{32}S (ISOFLEX: 99.99%) or ^{34}S (ISOFLEX: 99.26%) with a nominal composition of $Bi_4O_4S_3$. The mixed powder was pelletized, sealed in an evacuated quartz tube, and heated at 540 °C for 10 h. The obtained sample was examined by laboratory X-ray diffraction (XRD) by the θ-2θ method with a CuKα radiation on Miniflex600 (RIGAKU) equipped with a Dtex-Ultra semiconductor detector. Lattice constants were calculated by Rietveld fitting by RIETAN-FP [30]. The structural image was drawn by VESTA [31]. The temperature dependence of magnetization was measured by a superconducting quantum interference devise (SQUID) with an applied magnetic field of 10 Oe on MPMS-3 (Quantum Design). The temperature dependence of electrical resistivity was measured by a four-terminal method with an AC current of 1 mA on PPMS (Quantum Design). Au wires were attached on the sample surface by Ag paste. In this article, we have labeled the examined samples with the isotope mass (32 or 34) and alphabets (a–f) for clarity.

3. Results and discussion

We have synthesized polycrystalline samples at 540 °C because the reproducibility of the sample quality and the observed superconducting properties had been confirmed from experiments with natural sulfur chemical, while the obtained sample contained small amount of Bi_2S_3 and Bi impurities as indicated by + and * symbols as displayed in Fig. 1(a). Similar impurities were observed in previous reports on $Bi_4O_4S_3$ [13,27,29]. Since the crystal structure is complicated, as shown in Fig. 1(b), and there is possibility of stacking fault and modification of the stacking in the ternary Bi-O-S system [32-34], we have tried to synthesize $Bi_4O_4S_3$ isotope samples with close lattice constants to investigate the essential behavior on the isotope replacement between ^{32}S and ^{34}S. The lattice constants for the selected six samples are listed in Table I.

Figure 2 shows the temperature dependences of magnetization for $Bi_4O_4S_3$ samples with (a) ^{32}S and (b) ^{34}S. From the figure, the transition temperature in the magnetization data (T_c^M) looks almost the same. To evaluate T_c^M, temperature differential of magnetization (dM/dT) was calculated and plotted in Fig. 3. T_c^M was defined as a temperature where two linear fitting lines for the data just below and above the transition as shown in Fig. 3. The estimated T_c^M ranges from 4.73 to 4.76 K for ^{32}S and ^{34}S samples. Interestingly, there was no clear correlation between T_c^M and the isotope mass in the magnetization data. The isotope exponent calculated from all the

possible combination of T_c^M is -0.1 < α_S < 0.1.

Figure 4 shows the temperature dependences of electrical resistivity (ρ) for $Bi_4O_4S_3$ samples with (a) ^{32}S and (b) ^{34}S. Typically, a superconducting transition onset for $Bi_4O_4S_3$ is quite broad and obviously higher than zero-resistivity temperature, which was explained as strong superconducting fluctuation [35]. Therefore, the onset temperature is not preferable to be used for the discussion of isotope effect. We hence estimated resistive T_c (T_c^ρ) as a midpoint of the transition; the definition is displayed in Fig. 4(a). T_c^ρ was defined as a temperature where $\rho(T)$ becomes 50% of $\rho(T = 5$ K). As listed in Table I, T_c^ρ for ^{32}S samples ranges from 4.53 to 4.66 K, and T_c^ρ for ^{34}S samples ranges from 4.54 to 4.64 K. Although the T_c^ρ is relatively scattered as compared to the case of T_c^M, we could confirm that there is no clear correlation between T_c^ρ and the isotope mass.

As mentioned above, the Bi-O-S phases have various structural forms including stacking fault [32-34]. Here, to avoid the possibility of the shift in T_c due to those structural differences, we compare two (^{32}S and ^{34}S) samples having similar lattice constants. Accordingly, from table I, the set of #32-c and #34-e were selected. For those two samples, the T_c^Ms are the same ($T_c^M = 4.73$ K), and the T_c^ρs are 4.53 K for #32-c and 4.64 K for #34-e. If the conventional phonon-mediated mechanisms were essential in a superconductor with a $T_c = 4.7$ K, a difference in T_c of 0.14 K is expected between ^{32}S and ^{34}S isotopes. Therefore, the isotope effect seen from the comparison between #32-c and #34-e clearly deviates from the expectation from the conventional phonon-mediated superconductivity mechanisms. The present results show that the unconventional isotope effect is essential in $Bi_4O_4S_3$ with ^{32}S and ^{34}S.

Here, we briefly discuss about the commonality of the unconventional isotope effect in BiS_2-based superconductors. As mentioned in above, a similar unconventional isotope effect was observed in $LaO_{0.6}F_{0.4}BiSSe$ with BiSSe-type superconducting layers [26]. Although the constituent element of the superconducting layer is different, the in-plane structural symmetry is common because both are crystallized in a tetragonal structure ($P4/nmm$ for $LaO_{0.6}F_{0.4}BiSSe$ and $I4/mmm$ for $Bi_4O_4S_3$). In addition, T_c is close; the typical T_c of $LaO_{0.6}F_{0.4}BiSSe$ is 3.8 K. As well known, the BiS_2-based compounds exhibit a pressure-induced structural transition, at which a jump (abrupt increase) in T_c is observed [36-37]. In the case of $LaO_{0.5}F_{0.5}BiS_2$, T_c increases from 2 K (tetragonal $P4/nmm$) to 10 K (monoclinic ($P2_1/m$) by applying a pressure of 1 GPa [36]. Therefore, we can regard $LaO_{0.6}F_{0.4}BiSSe$ and $Bi_4O_4S_3$ with a tetragonal structure as a low-T_c phase of the BiS_2-based superconductor from a viewpoint of in-plane structural symmetry, which is also a commonality between those two superconductors. To conclude what factor is essential for the emergence of unconventional pairing states in the BiS_2-based superconductors, isotope effect and other studies for a high-T_c phase with a monoclinic phase is needed, and that is underway.

4. Conclusion

We have reported the sulfur isotope effect on T_c in $Bi_4O_4S_3$ with ^{32}S and ^{34}S. Polycrystalline samples of $Bi_4O_4S_3$ were prepared by solid-state reaction using ^{32}S and ^{34}S isotope chemicals. To investigate the isotope effect, six samples having similar lattice constants were selected. From magnetization analyses, the isotope exponent was estimated as $-0.1 < \alpha_S < 0.1$. Although the T_c estimated from electrical resistivity was scattered as compared to those estimated from the magnetization, we observed no clear correlation between T_c and the isotope mass. The present results on the isotope effect suggest $Bi_4O_4S_3$ to be an unconventional superconductor.

Reference

1. J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).
2. J. G. Bednorz, K. A. Müller, Z. Phys. B 64, 189 (1986).
3. Y. Kamihara, et al., J. Am. Chem. Soc. 130, 3296 (2008).
4. D. Pines, Physica C 235, 113 (1994).
5. A. Kreisel, et al., Phys. Rev. B 95, 174504 (2017).
6. D. G. Hinks et al., Nature 335, 419 (1988).
7. A. P. Ramirez et al. Phys. Rev. Lett. 68, 1058 (1992).
8. S. L. Bud'ko et al., Phys. Rev. Lett. 86, 1877 (2001).
9. D. D. Lawrie and J. P. Franck, Physica C 245, 159 (1995).
10. B. Batlogg et al., Phys. Rev. Lett. 58, 2333 (1987).
11. C. C. Tsuei et al., Phys. Rev. Lett. 65, 2724 (1990).
12. P. M. Shirage et al. Phys. Rev. Lett. 103, 257003 (2009).
13. Y. Mizuguchi et al., Phys. Rev. B 86, 220510 (2012).
14. Y. Mizuguchi et al., J. Phys. Soc. Jpn. 81, 114725 (2012).
15. Y. Mizuguchi, J. Phys. Soc. Jpn.88, 041001 (2019).
16. H. Usui and K. Kuroki, Nov. Supercond. Mater. 1, 50 (2015).
17. K. Suzuki, et al., J. Phys. Soc. Jpn. 88, 041008 (2019).
18. X. Wan et al., Phys. Rev. B 87, 115124 (2013).
19. S. F. Wu et al., Phys. Rev. B 90, 054519 (2014).

20. G. Lamura et al., Phys. Rev. B 88, 180509 (2013).

21. T. Yamashita et al., J. Phys. Soc. Jpn. 85, 073707 (2016).

22. C. Morice et al., Phys. Rev. B 95, 180505 (2017).

23. Y. Yang, et al., Phys. Rev. B 88, 094519 (2013).

24. A. Ichikawa and T. Hotta, J. Phys. Soc. Jpn. 87, 114706 (2018).

25. Y. Ota et al., Phys. Rev. Lett. 118, 167002 (2017).

26. K. Hoshi, Y. Goto, and Y. Mizuguchi, Phys. Rev. B 97, 094509 (2018).

27. S. K. Singh et al., J. Am. Chem. Soc 134, 16504 (2012).

28. H. Takatsu et al., J. Phys. Soc. Jpn. 81, 125002 (2012).

29. P. Srivatsava, Shruti, S. Patnaik, Supercond. Sci. Technol. 27, 055001 (2014).

30. F. Izumi and K. Momma, Solid State Phenom. 130, 15 (2007).

31. K. Momma and F. Izumi, J. Appl. Crystallogr. 41, 653 (2008).

32. A. Miura et al., Inorg. Chem., 54, 10462 (2015).

33. C. Morice et al., J. Phys.: Condens. Matter 27, 135501 (2015).

34. L. Li et al., Phys. Rev. B 91, 104511 (2015).

35. S. Li et al., Sci. China-Phys. Mech. Astron. 56, 2019 (2013).

36. C. T. Wolowiec et al., Phys. Rev. B 88, 064503 (2013).

37. T. Tomita et al., J. Phys. Soc. Jpn. 83, 063704 (2014).

Table I. Sample label, lattice constants, and T_c obtained from magnetization and resistivity (T_c^M and T_c^ρ) for $Bi_4O_4S_3$ samples with ^{32}S and ^{34}S.

Label	a (Å)	c (Å)	T_c^M (K)	T_c^ρ (K)
#32-a	3.9667(4)	41.337(5)	4.76	4.57
#32-b	3.9723(4)	41.367(6)	4.74	4.66
#32-c	3.9710(3)	41.368(4)	4.73	4.53
#34-d	3.9694(5)	41.358(6)	4.74	4.59
#34-e	3.9708(3)	41.361(4)	4.73	4.64
#34-f	3.9732(4)	41.384(4)	4.76	4.54

Figures

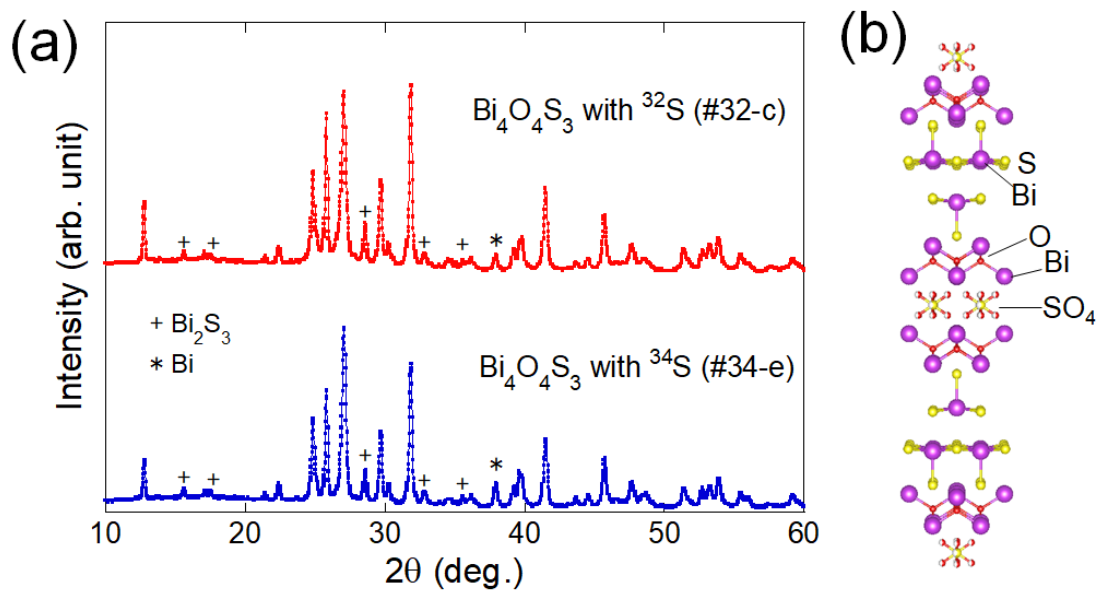Fig. 1. (a) X-ray powder diffraction for Bi₄O₄S₃ samples prepared with ^{32}S and ^{34}S isotope chemicals. (b) Schematic image of crystal structure of Bi₄O₄S₃.
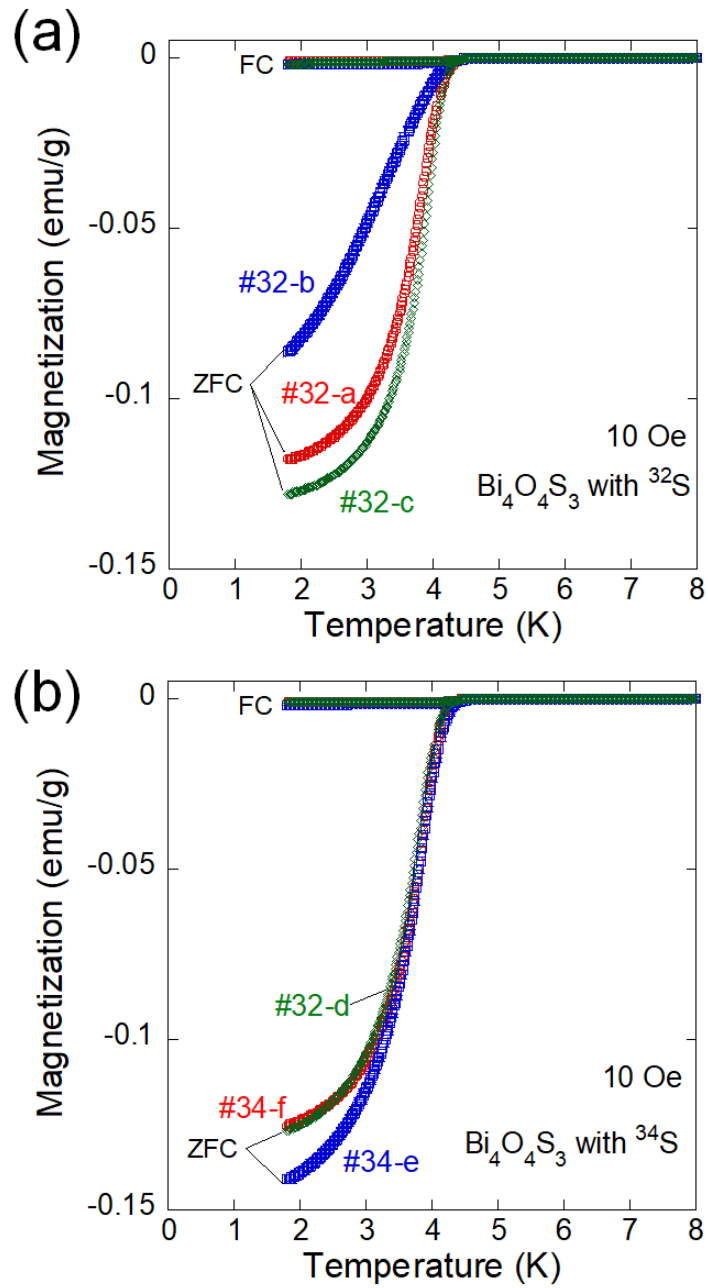
Fig. 2. Temperature dependences of magnetization after zero-filed cooling (ZFC) and field cooling (FC) for $Bi_4O_4S_3$ prepared with ^{32}S and ^{34}S.
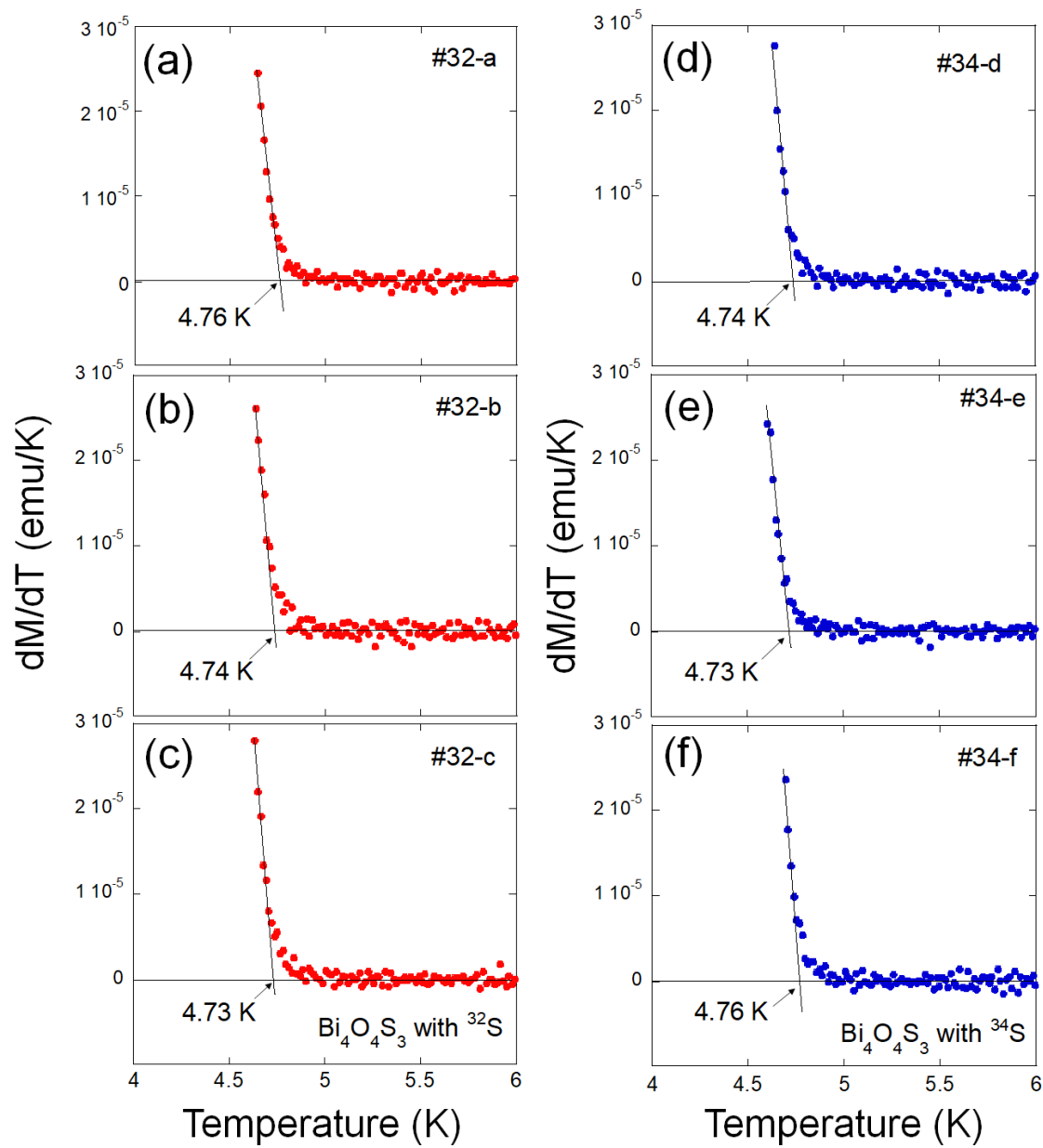
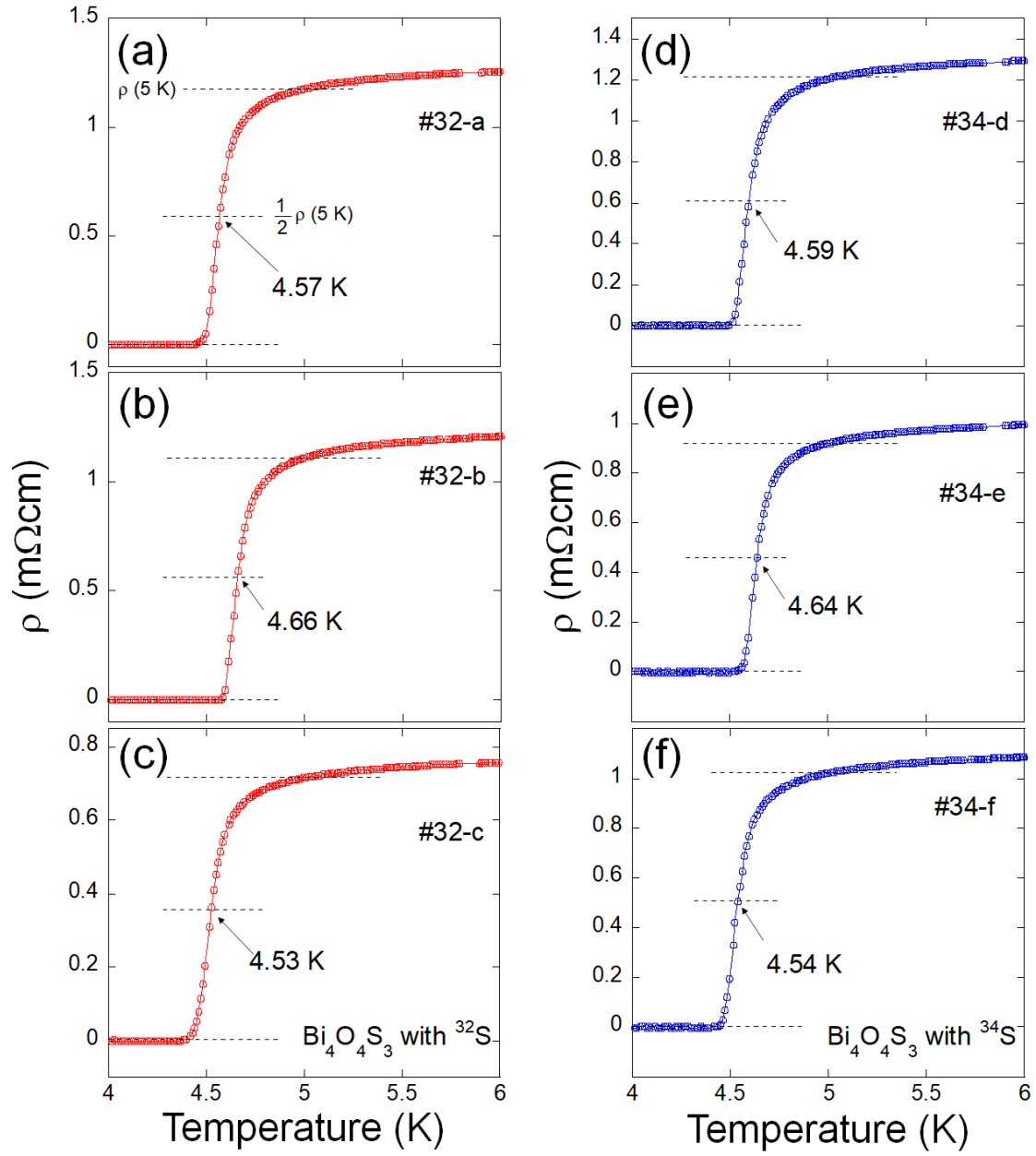Fig. 3. Temperature differential of magnetization (ZFC) for $Bi_4O_4S_3$ prepared with ^{32}S and ^{34}S.

Fig. 4. Temperature dependences of resistivity (ρ) for $Bi_4O_4S_3$ prepared with ^{32}S and ^{34}S.