

Bulk superconductivity in $\text{Bi}_4\text{O}_4\text{S}_3$ revealed by specific heat measurement

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(Received May 13, 2018)

KEYWORDS: $\text{Bi}_4\text{O}_4\text{S}_3$, Specific heat

Since the recent discovery of superconductivity in $\text{Bi}_4\text{O}_4\text{S}_3$, the BiS_2 -based superconducting family has attracted many researchers^{1–11)} because of some analogies to cuprates and Fe-based superconductors.^{12–14)} The parent phase of the $\text{Bi}_4\text{O}_4\text{S}_3$ superconductor is $\text{Bi}_6\text{O}_8\text{S}_5$ with a crystal structure composed of a stacking of BiS_2 layers (two BiS_2 layers) and $\text{Bi}_4\text{O}_4(\text{SO}_4)$ spacer layers.¹⁾ Band calculations^{1,9)} indicate that $\text{Bi}_6\text{O}_8\text{S}_5$ is an insulator with Bi^{3+} . Superconducting $\text{Bi}_4\text{O}_4\text{S}_3$ is expected to possess 50% defects at a SO_4 site, which generates electron carriers within the BiS_2 layers. In fact, superconductivity of $\text{Bi}_4\text{O}_4\text{S}_3$ is induced by electron doping into the BiS_2 layers via the defects of the SO_4 ions at the interlayer site.¹⁾ To date, LaOBiS_2 and NdOBiS_2 , having analogous BiS_2 layers, have been found to show superconductivity by electron doping as well.^{2,3)} Although the nature of superconductivity in the BiS_2 family has not been clarified so far, the relatively high transition temperature (T_c), for example, 10.6 K in $\text{La}(\text{O},\text{F})\text{BiS}_2$, attracts researchers to exploring new BiS_2 -based superconductors with a higher T_c . To elucidate the superconductivity mechanism or design new BiS_2 -based superconductors, it is important to clarify whether the observed superconductivity is bulk or occurred in surface. Here we show the evidence of bulk superconductivity in $\text{Bi}_4\text{O}_4\text{S}_3$ revealed by the specific heat measurements.

The polycrystalline $\text{Bi}_4\text{O}_4\text{S}_3$ sample was prepared by the conventional solid-state reaction method as described in Ref. 1. The sample quality was confirmed by the x-ray diffraction and dc susceptibility measurements. It was comparable to the result reported in Ref. 1. The T_c was estimated to be ~ 4.7 K. Specific heat was measured with a thermal relaxation method with a commercial calorimeter (PPMS, Quantum Design) down to 2 K.

Figure 1 shows the temperature dependence of the total specific heat C_P in the superconducting state ($\mu_0H = 0$ T) and in the normal-conducting state ($\mu_0H = 9$ T $> \mu_0H_c$). The C_P anomaly associated with the superconducting transition is observed, as indicated by the arrow ($T \simeq 4.7$ K). This result ensures that $\text{Bi}_4\text{O}_4\text{S}_3$ is a bulk superconductor. The tiny jump is attributed to the small electronic-specific-heat coefficient γ . Assuming the BCS weak coupling approximation, $\Delta C_P/\gamma T_c = 1.43$ and 100% superconducting volume, the γ value was yielded

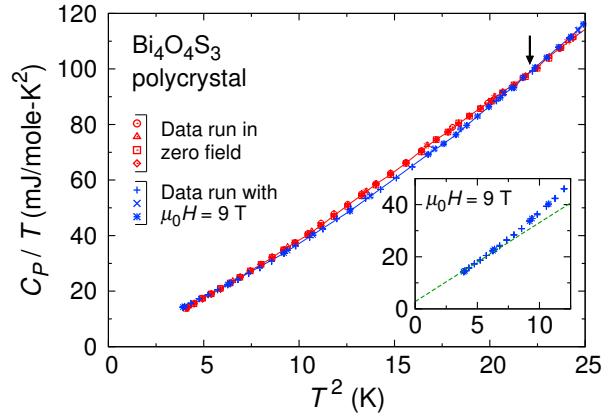


Fig. 1. Temperature dependence of total specific heat C_P of a polycrystalline sample of $\text{Bi}_4\text{O}_4\text{S}_3$. The inset shows the same C_P/T versus T^2 plot in the low- T region at 9 T (normal state).

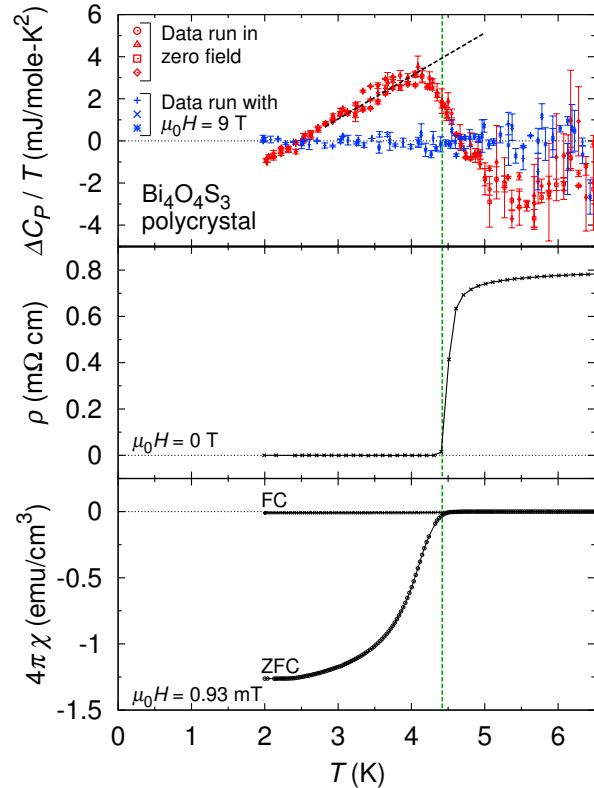


Fig. 2. Temperature dependence of (a) the difference in the electronic specific heat between the superconducting state and the normal-conducting state, $\Delta C_P = C_P(0\text{T}) - C_P(9\text{T})$, (b) resistivity ρ , and (c) dc magnetic susceptibility χ . The lines in (a) are entropy-conserving constructions in order to estimate the intrinsic jump height of ΔC_P . The transition temperature estimated by C_P is consistent with that from ρ and χ .

to be about 2.8 mJ/(f.u. mol K²). The inset of Fig. 1 presents the fitting result by a conventional relation, $C_P/T = \gamma + \beta T^2$, with the estimated γ and the coefficient of the phononic contribution β . Although lower- T data need to evaluate the certain γ value, the data is fairly fitted by the relation with $\beta = 3.0$ mJ/(f.u. mol K⁴) yielding the Debye temperature $\Theta_D = 192$ K. We expect that the small γ and low carrier⁴⁾ are essential

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for the superconducting mechanism of the BiS_2 -based superconductor.

From the intrinsic jump of C_P , we define the transition temperature $T_c = 4.4$ K in zero field, which agrees well with the temperature of the zero-resistivity and the starting temperature of the bifurcation between χ_{FC} and χ_{ZFC} . In Fig. 2, comparisons between those results are presented. For the C_P data, the difference in the electronic specific heat between the superconducting and normal-conducting states is estimated by a relation of $\Delta C_P = C_P(0\text{T}) - C_P(9\text{T})$, since the phononic contribution in C_P is usually H independent. We have fitted the 9 T data to a polynomial, and used it in calculating ΔC_P . We obtained the intrinsic jump height at T_c as $\Delta C_P/T_c = 4.0 \text{ mJ}/(\text{f.u. mol K}^2)$. We note that there is a small discrepancy between C_P data of the superconducting and normal-conducting states above T_c . However, this is only 2% of the total specific heat. Therefore, we think that this is not intrinsic in the nature of $\text{Bi}_4\text{O}_4\text{S}_3$, instead it is attributable to a small error of measurements or of the subtraction of the normal state contribution, because of the small specific heat jump.

In conclusion, our specific heat experiments on a polycrystalline sample of the BiS_2 -based superconductor $\text{Bi}_4\text{O}_4\text{S}_3$ demonstrate that the superconductivity of it is bulk in nature. The T_c is estimated by the specific heat measurements to be $T_c = 4.4$ K, consistent with that of the resistivity and dc susceptibility. In order to further discuss the superconductivity mechanism of $\text{Bi}_4\text{O}_4\text{S}_3$, lower temperature specific heat experiments below 2 K is essential.

Acknowledgment

We acknowledge Yusuke Nakai and Yoshihiko Takano for fruitful discussions and experimental supports. This work was partly supported by Grant-in-Aid for Research Activity Startup (23860042) from the Ministry of Education.

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