Evidence for nodeless superconductivity in NdO$_{1-x}$F$_x$BiS$_2$ ($x = 0.3$ and $0.5$) single crystals

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Abstract

We study the superconducting pairing states of NdO$_{1-x}$F$_x$BiS$_2$ ($x = 0.3$ and $0.5$) by measuring the magnetic penetration depth $\Delta \lambda(T)$ using the tunnel-diode-oscillator (TDO) technique. An upturn is observed in $\Delta \lambda(T)$ as well as the magnetic susceptibility $\chi(T)$ in the low-temperature limit, which is attributed to the paramagnetism of Nd ions. After subtracting the paramagnetic contributions, the penetration depth $\Delta \lambda(T)$ follows an exponential-type temperature dependence at $T \ll T_c$, providing evidence of nodeless superconductivity for NdO$_{1-x}$F$_x$BiS$_2$. This is further supported by the analyses of superfluid density $\rho_s(T)$, which can be well described by a BCS model with an energy gap of $\Delta(0) \sim 2.15 k_B T_c$.

Keywords: BiS$_2$-based superconductors, order parameter, London penetration depth

(Some figures may appear in colour only in the online journal)
showed evidence of an $s$-wave pairing symmetry. Recently, the successful growth of single crystalline NdO$_1$-$x$F$_x$BiS$_2$ provides us with a great opportunity to look into its pairing state in more detail [8, 9]. Here we present measurements of the magnetic penetration depth $\lambda(T)$ for NdO$_{1-x}$F$_x$BiS$_2$ ($x = 0.3$ and $0.5$) single crystals. The penetration depth $\lambda(T)$ and the corresponding superfluid density $\rho_s(T)$ are well described by a single-gap BCS model with moderate coupling, providing strong evidence of $s$-wave SC for NdO$_{1-x}$F$_x$BiS$_2$.

NdO$_{1-x}$F$_x$BiS$_2$ ($x = 0.3$ and $0.5$) single crystals were grown by using a flux method with CsCl/KCl as flux [8]. In this context, the F-concentration $x$ refers to the nominal values, which are close to the actual compositions as identified by the energy dispersion spectrum (EDX). Precise measurements of the penetration depth changes $\Delta\lambda(T)$ were performed by utilizing a TDO-based, self-inductive technique at an operating frequency of $7\,\text{MHz}$ down to $0.4\,\text{K}$ in a $^3\text{He}$ cryostat, with which we can obtain a noise level as low as $0.01\,\text{PPM}$. The magnetic penetration depth is proportional to the shift of the resonant frequency $\Delta f(T)$, i.e. $\Delta\lambda(T) = G\Delta f(T)$, where the $G$ factor is solely determined by the sample and coil geometries. For a square sample of side $2w$, thickness $2d$ and volume $V_c$, the $G$-factor can be estimated by: $G = 2R(1 - N)V_c/V_f$, where $R \approx w/2[1 + 1/(2d/w)^2]\arctan(w/2d) - 2d/w$ is the effective sample dimension, $N$ is the demagnetization factor, $V_c$ represents the coil volume, and $V_f$ is the TDO operating frequency [18]. The coil of the oscillator generates a tiny $ac$ magnetic field ($H_{ac} \approx 20\,\text{mOe}$), which is much smaller than the lower critical field of NdO$_{1-x}$F$_x$BiS$_2$ [19], ensuring that the measurements were performed in a Meissner state. The electrical resistivity and magnetic susceptibility were measured in a commercial Physical Properties Measurement System (PPMS) and Magnetic Properties Measurement System (MPMS), respectively.

In order to characterize the sample quality, we measured the temperature dependence of the electrical resistivity $\rho(T)$ and magnetic susceptibility $\chi(T)$ for NdO$_{1-x}$F$_x$BiS$_2$ ($x = 0.3$ and $0.5$), whose results are presented in figure 1. The electrical resistivity shows metallic behavior in the normal state for $T > 0.3$ and $x = 0.5$. The transition temperature $T_c$, determined from the mid-point of the sharp resistive transitions, is $4.7\,\text{K}$ and $4.4\,\text{K}$ for $x = 0.3$ and $0.5$, respectively. These $T_c$ values are very close to the onset transition temperature in the magnetic susceptibility $\chi(T)$. A superconducting volume of nearly $100\%$ is estimated for $x = 0.3$, while it is reduced to $70\%$ for $x = 0.5$. The NdO$_{1-x}$F$_x$BiS$_2$ system possesses a very small lower critical field ($\mu_0H_{c1}(0) \approx 25\,\text{Oe}$) [19], thus a tiny external magnetic field may significantly broaden the superconducting transition, as shown in figure 1(b). The inset of figure 1(b) shows the magnetic susceptibility $\chi(T)$ in the normal state, which can be fitted by the Curie–Weiss law, i.e. $\chi(T) = C/(T - \Theta)$. The derived Curie constants (Curie–Weiss temperatures) are $C = 0.0076\,\text{K}$ ($\Theta = -0.73\,\text{K}$) and $C = 0.0154\,\text{K}$ ($\Theta = -1.02\,\text{K}$) for $x = 0.3$ and $0.5$, respectively. Consequently, an effective moment of $\mu_{eff} \approx 1.97\,\mu_B$ and $2.80\,\mu_B$ is estimated for $x = 0.3$ and $0.5$, respectively, where $\mu_B$ is the Bohr magneton. Such Curie–Weiss behavior extends to the superconducting state as evidenced by the weak upturn of the magnetic susceptibility in the low-temperature limit (see figure 1(b)) and is likely attributed to the unpaired magnetic moments of Nd$^{3+}$ ions. The unpaired electrons can be affected by the local chemical environment and, therefore, the F/O substitutions or the Bi deficiency may lead to a change of the effective moments of Nd$^{3+}$ ions.

Measurements of the London penetration depth based on the TDO technique provide an important tool to probe the low-temperature excitations without an interference of magnetic field as typically encountered in the $\mu$SR and NMR experiments. In figure 2, we plot the temperature dependence of the resonant frequency shift $\Delta f(T)$ for $x = 0.3$ and $0.5$ with the $ac$ field generated along the $c$-axis; the inset expands the low-temperature part. The samples used in this measurement are with a typical size of $\sim 0.65 \times 0.65 \times 0.015\,\text{mm}^3$, which is difficult for the measurements with fields perpendicular to the $c$-axis. Thus, only the in-plane penetration depth is obtained in this context. In comparison with the magnetic susceptibility data, as shown in figure 1, a sharper superconducting transition
frequency shift $\Delta f(T)$ with decreasing temperature. The so-derived $T_c$s are close to the corresponding resistive values, and the sharp transition might be related to the negligible magnetic field generated in the TDO-based measurements. Therefore, the TDO-based measurements can provide a precise determination of $T_c$ for those superconductors with a tiny $\mu_0 H_{c1}(0)$. The consistency of the bulk and resistive $T_c$s suggest a good homogeneity of our samples.

From the inset of figure 2, one can see that $\Delta f(T)$ for $x = 0.3$ and 0.5 shows a pronounced upturn as temperature goes to zero. Similar behavior was previously observed in Nd$_{2−x}$Ce$_x$CuO$_4$−δ [20, 21], NdFeAsO$_{0.6}$F$_{0.4}$ [22] and SmFeAsO$_{1−x}$F$_x$ [23], which was attributed to the paramagnetic contributions of the magnetic ions. For superconductors with a significant paramagnetic background, the magnetic susceptibility in the Meissner state can be written as [21, 22]:

$$\chi(T) = \frac{\mu(T)}{\mu_0} \frac{\lambda(T)}{\lambda(0)} - 1,$$

where $\lambda(T)$ is the London penetration depth, $\mu(T)$ is the normal-state paramagnetic permeability, and $\lambda(0)$ is a characteristic sample dimension as defined above. In this case, the measured penetration depth is given by $\lambda(T) = \lambda_L(T) + \sqrt{\mu(T)}$, whose change is proportional to the shift of the resonant frequency $\Delta f(T)$.

For superconductors with an isotropic energy gap ($s$-wave) or a nodal gap structure, the changes of the effective penetration depth $\Delta \lambda(T) = G \Delta f(T) − \lambda_0$ at $T \ll T_c$ in the presence of paramagnetic contributions can be approximated by [22]:

$$\Delta \lambda(T) = \sqrt{\mu(T)} \lambda(0) \left( \frac{\pi \Delta(0)}{2k_B T} \right)^n \exp \left( - \frac{\Delta(0)}{k_B T} \right), \quad (1)$$

or

$$\Delta \lambda(T) \sim \sqrt{\mu(T)} \lambda(0) T^n, \quad (2)$$

where $\lambda(0)$ is the penetration depth at zero temperature, and $n = 1$ and 2 correspond to the cases of line nodes and point nodes in the superconducting energy gap, respectively.

In figure 2, the symbols plot the temperature dependence of the effective penetration depth $\Delta \lambda(T)$ for NdO$_{1−x}$F$_x$BiS$_2$, which are converted from the frequency shift $\Delta f(T)$ with $G = 7.4$ Å Hz$^{-1}$ and $7.8$ Å Hz$^{-1}$ for $x = 0.3$ and 0.5, respectively. The solid, dashed, and dotted lines represent the fits of the nodeless BCS model (equation (1)), the nodal gaps with line ($n = 1$), and point nodes ($n = 2$), respectively. In this context, we assume that the paramagnetism of Nd$^{3+}$ ions in the superconducting state still follows the Curie–Weiss behavior, i.e. $4\pi \chi_{Nd}(T) = 4\pi C/(T − \Theta) = \mu(T)$, with a constant magnetic moment (or the Curie constant $C$) and an adjusted Curie–Weiss temperature $\Theta$ while crossing the superconducting transition. It is noted that similar methods were previously applied to Nd$_{2−x}$Ce$_x$CuO$_4$−δ [20, 21], and the fits are poor if the same parameters of $C$ and $\Theta$ are adopted from the normal-state magnetic susceptibility. By taking $\lambda(0)$ as a free parameter, the fits of our experimental data by equation (1) give $\lambda(0) \approx 447$ nm and $480$ nm for $x = 0.3$ and 0.5, which are comparable to that of LaO$_{0.5}$F$_{0.5}$BiS$_2$ ($\lambda(0) = 484$ nm) obtained from the $\mu$SR measurements [17]. From figure 3, one can see that the experimental data deviate from the quadratic ($n = 2$) or the linear ($n = 1$) temperature dependence (equation (2)). Thus, it is unlikely that NdO$_{1−x}$F$_x$BiS$_2$ is of nodal superconductivity. On the other hand, the BCS model (equation (1)) fits nicely
Table 1. The fitting parameters of NdO$_{1-x}$F$_x$BiS$_2$ derived from the BCS model.

| $x$ | $T_c$(K) | $\Theta$(K) | $\lambda_L$(0) | $\Delta^s$(0) | $\Delta^p$(0) |
|-----|----------|-------------|----------------|--------------|--------------|
| 0.3 | 4.5      | -1.37       | 447            | 1.95         | 2.14         |
| 0.5 | 4.2      | -1.90       | 480            | 1.92         | 2.15         |

Figure 4. The normalized superfluid density $\rho_s(T)$ for NdO$_{1-x}$F$_x$BiS$_2$: (a) $x = 0.3$ and (b) $x = 0.5$. Various gap functions are plotted in the figures, i.e. $s$-wave SC (solid line), $p$-wave (dash-dotted line) and $d$-wave (dotted line).

to the experimental data of both $x = 0.3$ and 0.5; the fitting parameters are summarized in table 1. The derived superconducting gaps are $\Delta^s(0) = 1.95k_BT_c$ and $1.92k_BT_c$ for $x = 0.3$ and 0.5, respectively. These values are close to that of Bi$_4$O$_3$S$_3$ [15] and LaO$_{0.5}$F$_{0.5}$BiS$_2$ [17] obtained from the $\mu$SR experiments, but larger than that in the weak-coupling limit ($\Delta(0) = 1.76k_BT_c$), indicating moderate coupling SC in NdO$_{1-x}$F$_x$BiS$_2$.

To further analyze the gap symmetry, we derive the superfluid density $\rho_s(T)$ from the corresponding London penetration depth via $\rho_s(T) = \lambda_L(T)/\lambda_L(T_c)^2$ (see figure 4), where $\lambda_L(T)$ is obtained after subtracting the paramagnetic contributions. In general, the normalized superfluid density can be calculated by [18]:

$$\rho_s(T) = 1 + 2\int_{\Delta(T)}^{\infty} \frac{\partial f}{\partial E} \sqrt{\frac{E}{E^2 - \Delta_s^2(T)}} dE,$$

(3)

where $f = (e^{E/k_BT} + 1)^{-1}$ is the Fermi distribution function and $\langle \ldots \rangle_{FS}$ denotes the average over the Fermi surface. As an approximation, we assume that the temperature dependence of the energy gap $\Delta(T)$ follows BCS model [18]:

$$\Delta(T) = \Delta(0) \tanh \left( \frac{1.82}{0.51} \left( \frac{T_c}{T} - 1 \right) \right).$$

(4)

where $\Delta(0)$ is the energy gap at zero temperature. Given a gap function $\Delta(\theta, \phi) = \Delta(\theta, \phi) = [\sin(\theta)]^n$, Here we adopted a two-dimensional (2D) cylinder-like Fermi surface for the $s$- and $d$-wave models, and a spherical Fermi surface for the $p$-wave; the former one is in accordance with the ARPES results [24, 25]. One can see that the experimental data $\rho_s(T)$, which becomes saturated below $0.3T_c$, can be well fitted by the BCS model with an isotropic gap but apparently deviate from the other two models with nodes in the gap structure, providing further evidence of nodeless superconductivity for NdO$_{1-x}$F$_x$BiS$_2$. The derived superconducting energy gaps $\Delta^p(0)$ are listed in table 1, which are compatible with those obtained in the preceding analysis of the penetration depth $\lambda(T)$. It is noted that, for $x = 0.5$, the fit of the BCS model shows a small deviation from the experimental data $\rho_s(T)$ for $T > 0.7T_c$. At this stage, we cannot exclude the possibility of anisotropic or multiband superconductivity for $x = 0.5$, which may fit better to the experimental data (with more fitting parameters). On the other hand, such a small deviation might be caused by the uncertainties of the derived $\lambda_0$ and the $G$-factor too.

The above analyses of the magnetic penetration depth $\Delta(\theta)$ and the corresponding superfluid density $\rho_s(T)$ have shown fully-gapped superconductivity for NdO$_{1-x}$F$_x$BiS$_2$ ($x = 0.3$ and 0.5). Evidence of nodeless superconductivity was also observed in Bi$_4$O$_3$S$_3$ [15, 16] and LaO$_{0.5}$F$_{0.5}$BiS$_2$ [17], in which the paramagnetic contributions of Nd$^{3+}$ are absent. This suggests that a nodeless gap structure is a common feature of the Bi$_2$S$_2$-superconductors. In a conventional $s$-wave superconductor, $T_c$ can be rapidly suppressed by magnetic scattering [26]. Thus, the appearance of fully-gapped SC in the presence of Nd magnetic moments is unusual. Indeed, evidence of nodal superconductivity was shown for the Nd-based superconductors Nd$_2$CuO$_4$S$_3$ [20, 21] and NdFeAsO$_{0.9}$F$_{0.1}$ [22]. Recently, it was theoretically proposed that, as a result of strong spin–orbit coupling, a dominant spin-triplet state may coexist with a spin-singlet component in the Bi$_2$S$_2$-based superconductors, resulting in a crossover from nodeless SC to nodal SC with increasing the electron filling above the so-called Lifshitz point [13]. If such a theoretical scenario is valid, then our results suggest that the filling level of NdO$_{0.5}$F$_{0.5}$BiS$_2$ is still below the Lifshitz point, and nodal SC would be expected with further increasing the F-doping concentration, which might push the Fermi level close to a van Hove singularity. Indeed, the recent ARPES experiments revealed that the deficiency of Bi element in

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NdO$_1$-$x$F$_x$BiS$_2$ may result in a reduction of the actual filling level [24], meaning that the samples with $x = 0.5$ are possibly below the Lifshitz point. Therefore, it is highly desirable to systematically study the samples with higher doping concentrations. Unfortunately, the growth of single crystals with rich F-content has not been successful yet and further efforts are badly needed. On the other hand, the coexistence of $s$-wave superconductivity and magnetic order was also evidenced in the layered nickel borocarbides RNi$_2$B$_2$C ($R =$ rare earth) [27]. It is possible that the interactions between the magnetic layers (NdO layer in our case) and the conducting layers are not strong enough to suppress superconductivity. Nevertheless, no evidence of long-range magnetic order was found in our NdO$_1$-$x$F$_x$BiS$_2$ samples.

In summary, we have performed measurements of magnetic penetration depth $\Delta \lambda(T)$ for the NdO$_1$-$x$F$_x$BiS$_2$ ($x = 0.3$ and $0.5$) single crystals by utilizing a TDO-based technique down to 0.4 K. Both the penetration depth $\lambda(T)$ and the superfluid density $\rho_s(T)$ get saturated at $T \ll T_c$, and their temperature dependence can be described in terms of the BCS model. These findings strongly suggest nodeless superconductivity for NdO$_1$-$x$F$_x$BiS$_2$. Future works are needed to reveal the evolution of the gap structure at various dopings, in particular in the overdoped region, which may provide essential insights into the recently developed theoretical models for the BiS$_2$-based superconductors.

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