

Pressure-induced enhancement of superconductivity and suppression of semiconducting behavior in $LnO_{0.5}F_{0.5}BiS_2$ ($Ln = La, Ce$) compounds

C. T. Wolowiec,^{1,2} D. Yazici,^{1,2} B. D. White,^{1,2} K. Huang,^{1,2,3,*} and M. B. Maple^{1,2,3,*}¹*Department of Physics, University of California, San Diego, La Jolla, California 92093, USA*²*Center for Advanced Nanoscience, University of California, San Diego, La Jolla, California 92093, USA*³*Materials Science and Engineering Program, University of California, San Diego, La Jolla, California 92093, USA*

(Received 20 May 2013; revised manuscript received 15 July 2013; published 9 August 2013)

Electrical resistivity measurements as a function of temperature between 1 and 300 K were performed at various pressures up to 3 GPa on the superconducting layered compounds $LnO_{0.5}F_{0.5}BiS_2$ ($Ln = La, Ce$). At atmospheric pressure, $LaO_{0.5}F_{0.5}BiS_2$ and $CeO_{0.5}F_{0.5}BiS_2$ have superconducting critical temperatures T_c of 3.3 and 2.3 K, respectively. For both compounds, the superconducting critical temperature T_c initially increases, reaches a maximum value of 10.1 K for $LaO_{0.5}F_{0.5}BiS_2$ and 6.7 K for $CeO_{0.5}F_{0.5}BiS_2$, and then gradually decreases with increasing pressure. Both samples also exhibit transient behavior in the region between the lower T_c phase near atmospheric pressure and the higher T_c phase at higher pressures. This region is characterized by a broadening of the superconducting transition, in which T_c and the transition width ΔT_c are reversible with increasing and decreasing pressure. There is also an appreciable pressure-induced and hysteretic suppression of semiconducting behavior up to the pressure at which the maximum value of T_c is found. At pressures above the value at which the maximum in T_c occurs, there is a gradual decrease of T_c and further suppression of the semiconducting behavior with pressure, both of which are reversible.

DOI: 10.1103/PhysRevB.88.064503

PACS number(s): 61.50.Ks, 74.25.F-, 74.62.Fj, 74.70.Dd

I. INTRODUCTION

Superconductivity with a superconducting critical temperature $T_c = 8.6$ K has recently been reported in the layered compound $Bi_4O_4S_3$.^{1,2} Following this report, other BiS_2 -based superconductors including $LnO_{1-x}F_xBiS_2$ ($Ln = La, Ce, Pr, Nd, Yb$) with a T_c as high as 10.6 K have been synthesized and studied.^{3–12} More recent work demonstrates that chemical substitution of the tetravalent ions Th^{+4} , Hf^{+4} , Zr^{+4} , and Ti^{+4} for trivalent lanthanum, La^{+3} , in $LaOBiS_2$ increases the charge-carrier density and induces superconductivity.¹³ Most of the research on the layered BiS_2 compounds has heretofore centered on the effect of chemical substitution on superconductivity. Application of an external pressure may also be employed as a method for reducing the unit cell volume of these compounds and studying the resultant effect on superconductivity. In this paper, we report measurements of the pressure dependence of the normal state electrical resistivity between 1 and 300 K and T_c at various pressures up to ~ 3 GPa for the compounds $LaO_{0.5}F_{0.5}BiS_2$ and $CeO_{0.5}F_{0.5}BiS_2$. We compare our results to recently reported studies of $LaO_{0.5}F_{0.5}BiS_2$ samples synthesized under high pressure by Kotegawa *et al.*⁷

The qualitative evolution of T_c with pressure is markedly similar for both $LaO_{0.5}F_{0.5}BiS_2$ and $CeO_{0.5}F_{0.5}BiS_2$, which have T_c values (at atmospheric pressure) of 3.3 and 2.2 K, respectively. For both compounds, T_c initially increases, reaches a maximum value of 10.1 K at ~ 1 GPa for $LaO_{0.5}F_{0.5}BiS_2$ and 6.7 K at ~ 2 GPa for $CeO_{0.5}F_{0.5}BiS_2$, and then gradually decreases with increasing pressure. Both compounds also exhibit striking transient behavior in the region between the lower T_c phase near atmospheric pressure and the higher T_c phase at higher pressures. This transient region is characterized by a rapid increase of T_c and an increase of the superconducting transition width ΔT_c , in which both T_c and ΔT_c are reversible with increasing and decreasing pressure cycles. This occurs over a range in

pressure from ~ 0.5 to 1.1 GPa for $LaO_{0.5}F_{0.5}BiS_2$ and from ~ 0.5 to 1.5 GPa for $CeO_{0.5}F_{0.5}BiS_2$. In both materials, there is a sizable pressure-induced suppression of semiconducting behavior exhibiting hysteresis up to the pressure at which the maximum value of T_c is found. The rapid increase of the charge carrier density inferred from the suppression of the semiconducting behavior correlates with the rapid increase of T_c in this region. At pressures above the value at which the maximum in T_c occurs, there is a gradual decrease of T_c and further suppression of the semiconducting behavior with pressure, both of which are reversible.

II. EXPERIMENTAL DETAILS

Polycrystalline samples of $LnO_{1-x}F_xBiS_2$ ($Ln = La, Ce$) with $x = 0.5$ were prepared by solid-state reaction using powders of La_2O_3 (99.9%), LaF_3 (99.9%), La_2S_3 (99.9%), and Bi_2S_3 (99.9%) for $LaO_{1-x}F_xBiS_2$, and powders of CeF_3 (99.9%) and CeO_2 (99.9%) for $CeO_{1-x}F_xBiS_2$. Bi_2S_3 precursor powder was prepared in an evacuated quartz tube by reacting Bi (99.99%) and S (99.99%) at 500 °C for 10 hours. The Ln_2S_3 ($Ln = La, Ce$) precursor powders were prepared in an evacuated quartz tube by reacting chunks of La and Ce with S grains at 800 °C for 12 hours. The starting materials with nominal composition $LnO_{0.5}F_{0.5}BiS_2$ ($Ln = La, Ce$) were weighed, thoroughly mixed, pressed into pellets, sealed in evacuated quartz tubes, and annealed at 800 °C for 10 hours. The products were then ground, mixed for homogenization, pressed into pellets, and annealed again in evacuated quartz tubes at 800 °C for 10 hours. X-ray powder diffraction measurements were made using an x-ray diffractometer with a Cu K_α source to assess phase purity and to determine the crystal structure of the $LnO_{0.5}F_{0.5}BiS_2$ ($Ln = La, Ce$) compounds. Lattice parameters for $LaO_{0.5}F_{0.5}BiS_2$ are $a = 4.0613$ Å and $c = 13.3157$ Å, while for $CeO_{0.5}F_{0.5}BiS_2$ the lattice parameters are $a = 4.0398$ Å and $c = 13.4513$ Å.¹²

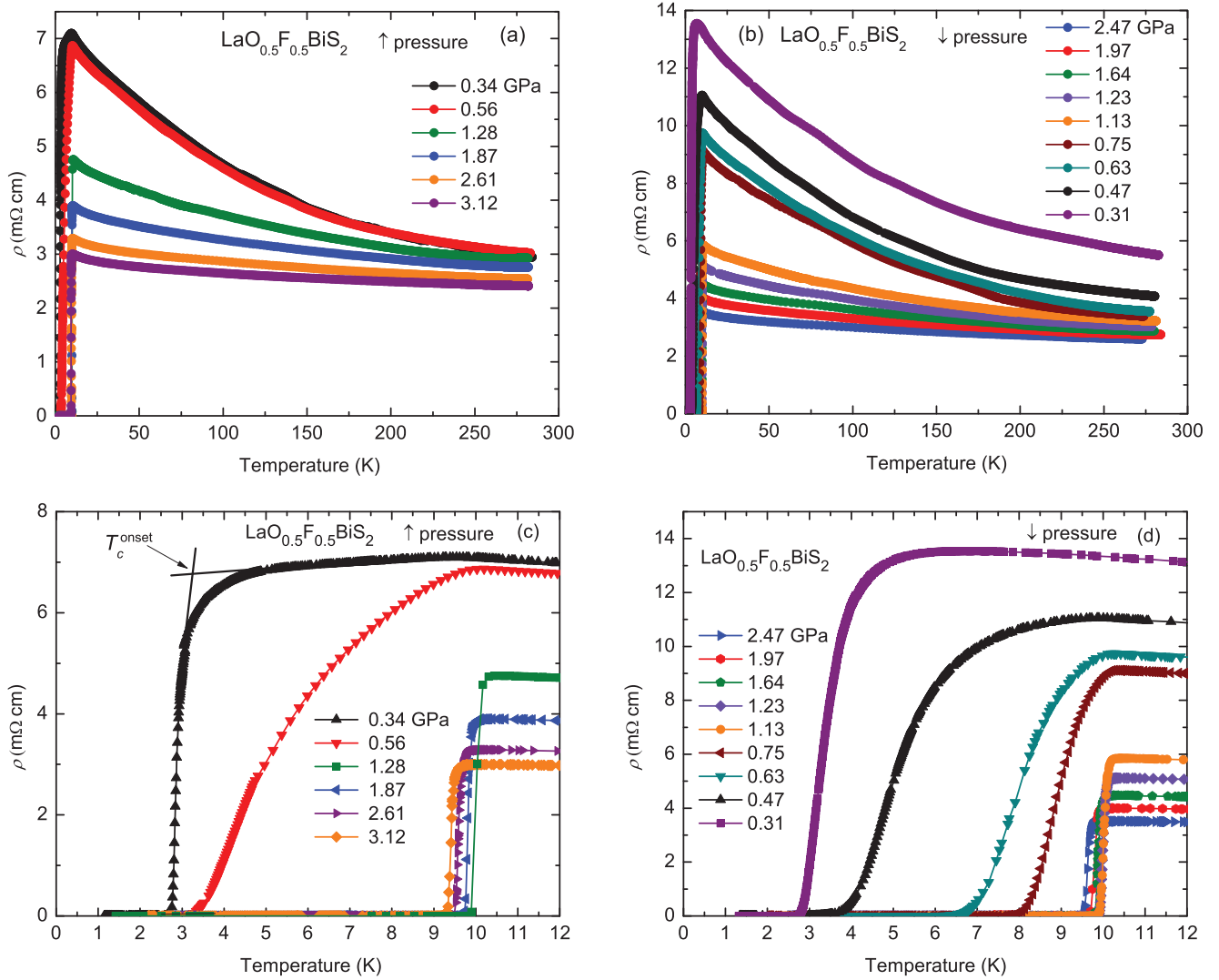


FIG. 1. (Color online) (a), (b) Temperature dependence of electrical resistivity ρ for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ at various pressures upon (a) increasing and (b) decreasing pressure. The electrical resistivity $\rho(T)$ is suppressed with increasing pressure as seen from the flattening of the curves at higher pressure. (c), (d) Resistive superconducting transition curves for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ upon (c) increasing and (d) decreasing pressure. T_c increases from 2.9 K to a maximum of 10.1 K before gradually decreasing.

Measurements of $\rho(T)$ under applied pressure were performed up to ~ 3 GPa in a clamped piston cylinder pressure cell between ~ 1 and 300 K in a pumped ^4He dewar. A 1:1 by volume mixture of *n*-pentane and isoamyl alcohol was used to provide a quasihydrostatic pressure transmitting medium. A second set of electrical resistivity measurements were performed by releasing pressure from the pressurized cell down to atmospheric pressure. Annealed Pt leads were affixed to gold-sputtered contact surfaces on each sample with silver epoxy in a standard four-wire configuration. The pressure dependent superconducting T_c of high purity Sn, measured inductively, was used as a manometer and calibrated against data from Ref. 14.

III. RESULTS AND DISCUSSION

The temperature dependence of the electrical resistivity ρ below 300 K for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ at various pressures is

displayed in Fig. 1. Figure 1(a) shows $\rho(T)$ upon increasing pressure to 3.1 GPa, while Fig. 1(b) gives $\rho(T)$ upon decreasing pressure back down to 0.31 GPa. The temperature dependence of $\rho(T)$ at lower pressures exhibits semiconducting behavior. The semiconducting behavior is suppressed with increasing pressure as seen from the nearly constant $\rho(T)$ curves above 2 GPa. A comparison of Fig. 1(a) with Fig. 1(b) shows that the suppression of $\rho(T)$ is continuous and reversible over the full range 0.3–3.1 GPa. At pressures above 2 GPa where suppression is greatest, the values of $\rho(T)$ are comparable in Figs. 1(a) and 1(b) and reversible with pressure. However, whereas the suppression of $\rho(T)$ is reversible with pressure, the magnitude of $\rho(T)$ exhibits hysteretic behavior with pressure. At lower pressures, measurements of $\rho(T)$ made during release of pressure yield higher values than $\rho(T)$ measurements performed upon increasing pressure. The difference between $\rho(T)$ measurements made during increasing pressure and those made during decreasing pressure

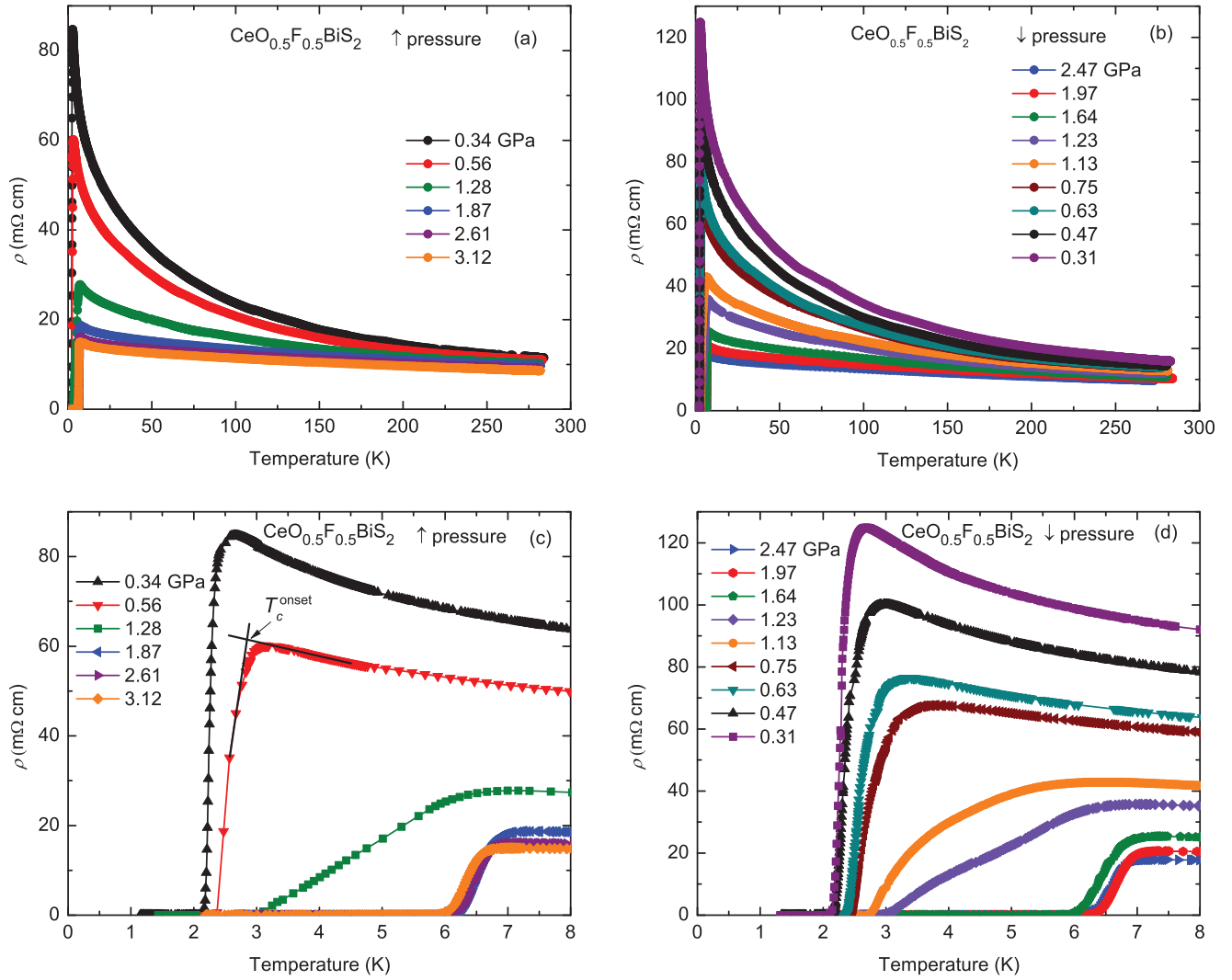


FIG. 2. (Color online) (a), (b) Temperature dependence of electrical resistivity ρ for $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ at various pressures upon (a) increasing pressure and (b) decreasing pressure. At lower pressures, the compound exhibits semiconducting behavior. The semiconducting behavior is suppressed at higher pressure as seen from the flattening of the curves. (c), (d) Resistive superconducting transition curves for $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ at various pressures upon (c) increasing and (d) decreasing pressure. T_c increases from 2.3 K to a maximum of 6.7 K and then gradually decreases.

are largest at lower pressures where the rate of suppression of semiconducting behavior is largest. After a release in pressure to the lowest value of 0.31 GPa, the maximum value of ρ is nearly 14 $\text{m}\Omega \text{ cm}$. This is a factor of 2 larger than the corresponding value along the increasing pressure path at 0.34 GPa.

Superconducting transitions at low temperature were measured upon increasing and then releasing pressure as shown in Figs. 1(c) and 1(d), respectively. There is a striking similarity in the qualitative behavior and evolution of the transitions in both plots. For pressures in the range 0.5 to 1.0 GPa, the superconducting transitions broaden significantly. For higher pressures above 1.0 GPa, the transition curves begin to sharpen again at approximately 10 K. It is in this higher pressure region where T_c passes through a maximum of 10.1 K at ~ 1 GPa and then gradually decreases as pressure increases. The evolution of both the value of the superconducting critical temperature T_c and the superconducting transition ΔT_c defined by the procedure described in the text, were reversible with respect

to both increasing and decreasing pressure. T_c was defined as the temperature at which ρ falls to 50% of its value at the temperature of the onset of superconductivity T_c^{onset} with T_c^{onset} determined as illustrated in Fig. 1(c). The temperature where the resistivity vanishes T_0 was determined in a similar fashion as T_c^{onset} using a linear extrapolation of the resistive superconducting curve to $\rho = 0$. In determining T_c for the broader transitions, we used the same criteria as for the sharper transitions; however, we make note of the less definitive T_c for these broader transitions.

Measurements performed on $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ reveal remarkably similar behavior to the $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ results. As shown in Fig. 2, the qualitative behavior of the results are reversible upon application and release of pressure. Measurements of $\rho(T)$ show semiconducting behavior which is suppressed at higher pressures. As pressure is released, the semiconducting behavior is recovered. The measured values of $\rho(T)$ are higher along the reversed path during a release of pressure. The discrepancy between $\rho(T)$ measurements made

during increasing pressure and those made during decreasing pressure are largest at lower pressures where the rate of suppression of the semiconducting behavior is largest. After releasing the pressure to the lowest value of 0.31 GPa, ρ is nearly 130 m Ω cm; this is a factor of 1.5 larger than the corresponding value along the increasing pressure path at 0.34 GPa.

Superconducting transitions at low temperature were measured for $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ while increasing and then decreasing pressure. The trend and character of the transitions are reversible upon application and subsequent release of pressure as seen from a comparison of Figs. 2(c) and 2(d). Similar to the evolution of T_c in $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$, sharp superconducting transitions are observed at low pressures up to approximately 0.5 GPa before they begin to broaden. From both the increasing and decreasing pressure plots [Figs. 2(c) and 2(d), respectively], the transitions begin to broaden significantly up to pressures of approximately 1.5 GPa. At pressures above 1.5 GPa, the superconducting transitions become sharp again. It is in this pressure region where T_c passes through a maximum of 6.7 K at ~ 2 GPa and then decreases gradually at higher pressures.

Figure 3 summarizes the results for the superconducting phase diagram $T_c(P)$ for both the $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ and $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ compounds. The measurements were performed first by increasing the pressure monotonically in six steps (filled symbols) up to 3.1 GPa, followed by a monotonic decrease in pressure in nine steps (open symbols) back down to 0.31 GPa. The phase diagram indicates $T_c(P)$ is highly reversible for both compounds; negligible pressure hysteresis is observed even in the regions where the resistive transition broadens significantly.

The phase diagram in Fig. 3 shows T_c maxima for both the $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ and $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ compounds. In the case of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$, T_c initially increases with pressure up to a maximum of 10.1 K at 1.1 GPa. T_c then gradually decreases with a slope of -0.30 K GPa $^{-1}$. This T_c maximum is also preceded by a reversible broadening of the superconducting transition in the pressure range 0.5–1.0 GPa, represented as elongated vertical bars in Fig. 3. In the normal state [above the $T_c(P)$ curve], the semiconducting behavior of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ is continuously suppressed with pressure as manifested in an energy gap Δ_1 that decreases with pressure, the values of which are indicated in the legend. The determination of the energy gaps Δ_1 and Δ_2 from the $\rho(T, P)$ data are discussed below. This maximum in $T_c(P)$ at 1.1 GPa occurs in the vicinity of a change of slope in the normal state $\log(\rho)$ vs P relation, measured at 11 K, as shown in Fig. 4.

In the case of $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$, T_c initially increases to a maximum of 6.7 K at ~ 2 GPa and then decreases slowly with a slope of -0.30 K GPa $^{-1}$ at higher pressures. Leading up to this maximum is a reversible broadening of the superconducting transition in the region 0.5–1.5 GPa depicted by the lengthened vertical bars in Fig. 3. In the normal state [above the $T_c(P)$ curve], the semiconducting behavior of $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ is also continuously suppressed with pressure as manifested in an energy gap Δ_1 that decreases with pressure, the values of which are indicated in the legend. The maximum in $T_c(P)$ at 2 GPa also occurs in the vicinity of a slope change in $\log(\rho)$ vs P , measured at 7.6 K, as shown in Fig. 4.

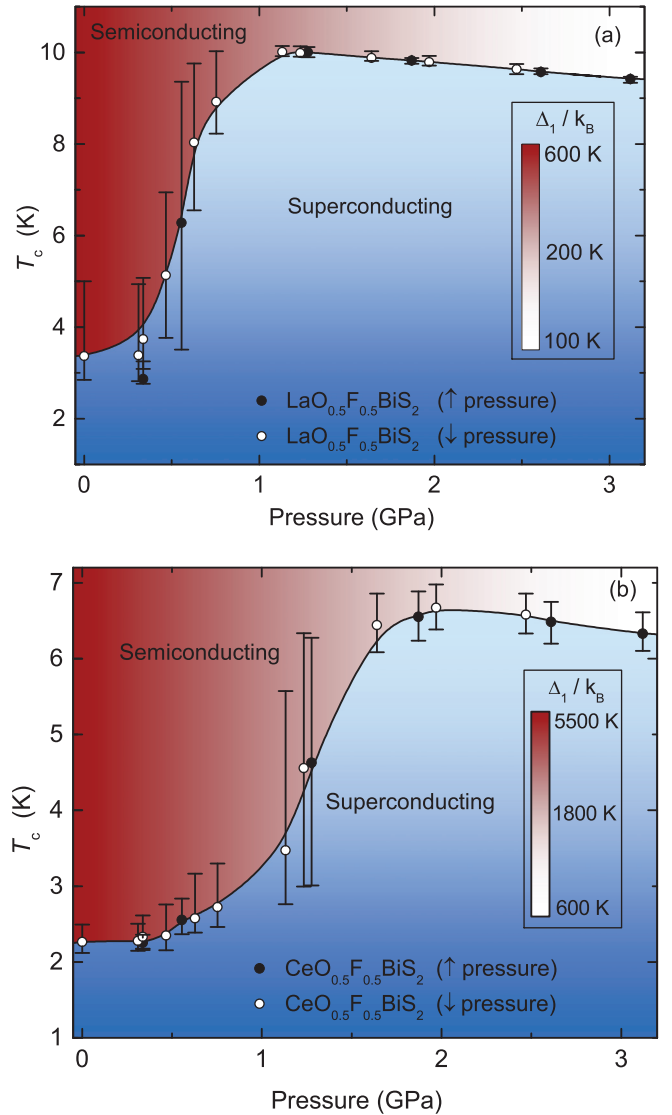


FIG. 3. (Color online) Phase diagrams for (a) $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ and (b) $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ under pressure. T_c was defined as the temperature at which the electrical resistivity ρ falls to 50% of its value at the temperature of the onset of superconductivity T_c^{onset} . The length of the vertical bars indicate the superconducting transition width ΔT_c and vertical bar caps indicate T_c^{onset} (upper) and T_0 (lower). Filled symbols denote measurements performed upon increasing pressure, while open symbols represent measurements made upon decreasing pressure. The solid black curves are guides to the eye. The change in color in the semiconducting normal state region represents the suppression of the semiconducting behavior with pressure as manifested in the decrease of the energy gap Δ_1 whose values are indicated in the legend.

The width of the superconducting transitions in the broadening region, represented by the length of the vertical bars in Fig. 3, is $\Delta T_c \sim 4$ –6 K. Pressure gradients in the piston-cylinder cell were estimated from the error in pressure to be of the order $\Delta P \sim \pm 0.05$ GPa where the error in pressure was determined from the width of the superconducting transition of the Sn manometer. It is possible to relate ΔT_c and ΔP through the slope of $T_c(P)$ in Fig. 3 so that $\Delta T_c \simeq (dT_c(P)/dP)\Delta P$. Even though ΔP is small

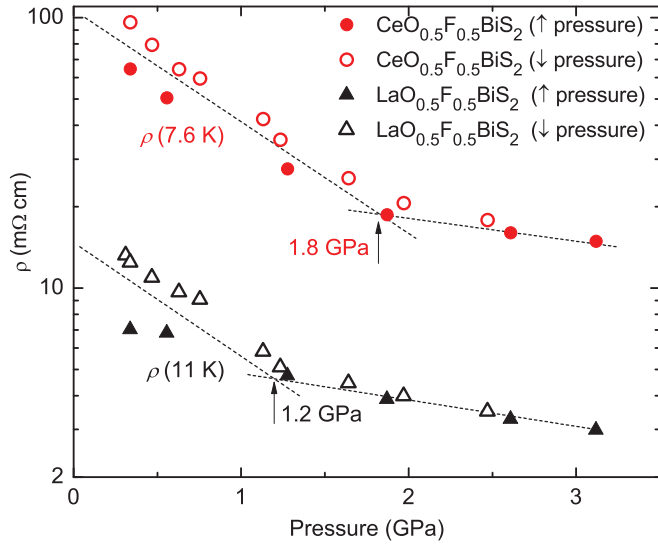


FIG. 4. (Color online) Electrical resistivity ρ in the normal state just above the superconducting onset temperature T_c^{onset} . Electrical resistivity values for $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ were taken at $T = 7.6$ K, while ρ values for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ were taken at $T = 11$ K. Filled (open) symbols represent measurements upon increasing (decreasing) pressure. Dotted lines reflect the slopes (suppression rates), and arrows point to changing slopes at ~ 1.2 GPa and ~ 1.8 GPa in $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ and $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$, respectively. The break in slope occurs at a pressure near that at which T_c reaches a maximum for both $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ and $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$.

and constant for pressures measured as part of this study, ΔT_c can be large when $dT_c(P)/dP$ is large (i.e., in the pressure region where broadened transitions are observed). Rough estimates of ΔT_c were made using $\Delta P = 0.1$ GPa and slopes of 18 and 11 K/GPa for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ and $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$, respectively. These calculations yield values of $\Delta T_c = 1.8$ and 1.1 K for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ and $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$, respectively, which are of the correct order of magnitude. The size of the vertical bars characterizing ΔT_c also appear to qualitatively track with the local slope of $T_c(P)$ for most pressures in Fig. 3.

Kotegawa *et al.*⁷ previously reported the pressure dependence of T_c for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ samples synthesized under high pressure, which apparently exhibit only the high T_c phase uncovered in the present study. In their experiments, it was found that T_c exhibits a maximum of 10.6 K at ~ 1 GPa and then gradually decreases with a slope of -0.40 K/GPa (compared to -0.30 K/GPa in this study) at pressures above 1 GPa. The low T_c phase and broadened superconducting transitions bridging the low T_c and high T_c phases, however, are not present in their $T_c(P)$ phase diagram. The presence of only the high T_c phase at ambient pressure in the study by Kotegawa *et al.*⁷ suggests that synthesis of the $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ samples under high pressure has already induced the high T_c superconducting phase.

From the plot of $\log(\rho)$ vs P at low temperature displayed in Fig. 4, there is a noticeable change in the magnitude of the suppression rate $d\log(\rho)/dP$ for both the $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ and $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ compounds. In the case of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$, there is a strong suppression of resistivity up to ~ 1.2 GPa, followed by a weaker suppression at higher pressures. In the case of $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$, there is a strong suppression of

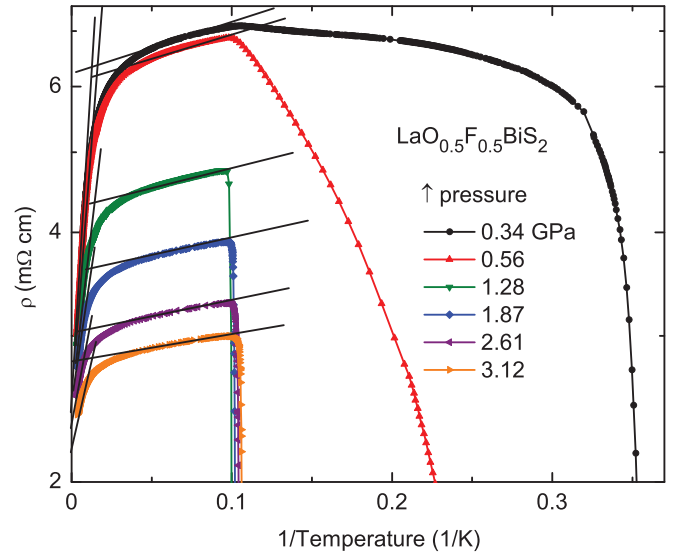


FIG. 5. (Color online) $\log(\rho)$ vs $1/T$ up to 3.12 GPa for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$. The solid lines represent linear fits of Eq. (1) which were used to determine the high and low temperature energy gaps Δ_1 and Δ_2 , respectively.

resistivity up to ~ 1.8 GPa, followed by a weaker suppression at higher pressures. The $\rho(P)$ data for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ and $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ were taken in the normal state at 11 and 7.6 K, respectively. These temperatures occur just above the onset of the superconducting transition at T_c^{onset} . The dotted lines in Fig. 4 are guides to the eye for the rates of suppression of $\log(\rho)$ with pressure.

There is a correlation between the pressure at which the maximum T_c occurs in the $T_c(P)$ phase diagram of Fig. 3 and the pressure where the suppression rate changes in the plot of $\log(\rho)$ vs P in Fig. 4. For $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$, this “critical pressure” occurs at ~ 1.2 GPa, while for $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ it is located at ~ 1.8 GPa. In both compounds, there is also an apparent pressure hysteresis as seen from the separation between the increasing pressure data (open symbols) and the decreasing pressure data (filled symbols). This pressure hysteresis becomes more pronounced where the suppression rate is higher, i.e., below the previously mentioned critical pressures.

The semiconducting behavior of the $\rho(T)$ data and its rapid suppression with pressure was noted in the work of Kotegawa *et al.*⁷ on the $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ compound synthesized under high pressure. They observed that the resistivity could be described over two distinct regions by the relation

$$\rho(T) = \rho_0 e^{\Delta/2k_B T}, \quad (1)$$

where ρ_0 is a constant and Δ is an energy gap. Analysis of the $\rho(T)$ data at atmospheric pressure in these two regions, 200–300 K and $T_c - 20$ K, yielded energy gaps $\Delta_1/k_B \approx 140$ and $\Delta_2/k_B \approx 1.86$ K, respectively. Both energy gaps Δ_1 and Δ_2 were found to decrease with pressure. In this study, we have also determined values of the energy gaps Δ_1 and Δ_2 from linear fits of $\rho(T)$ data on a plot of $\log(\rho)$ vs $1/T$, as illustrated in Fig. 5, which displays our $\rho(T)$ data for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ upon increasing pressure. From similar plots for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ upon decreasing pressure as well as for $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ upon increasing and decreasing pressure, the

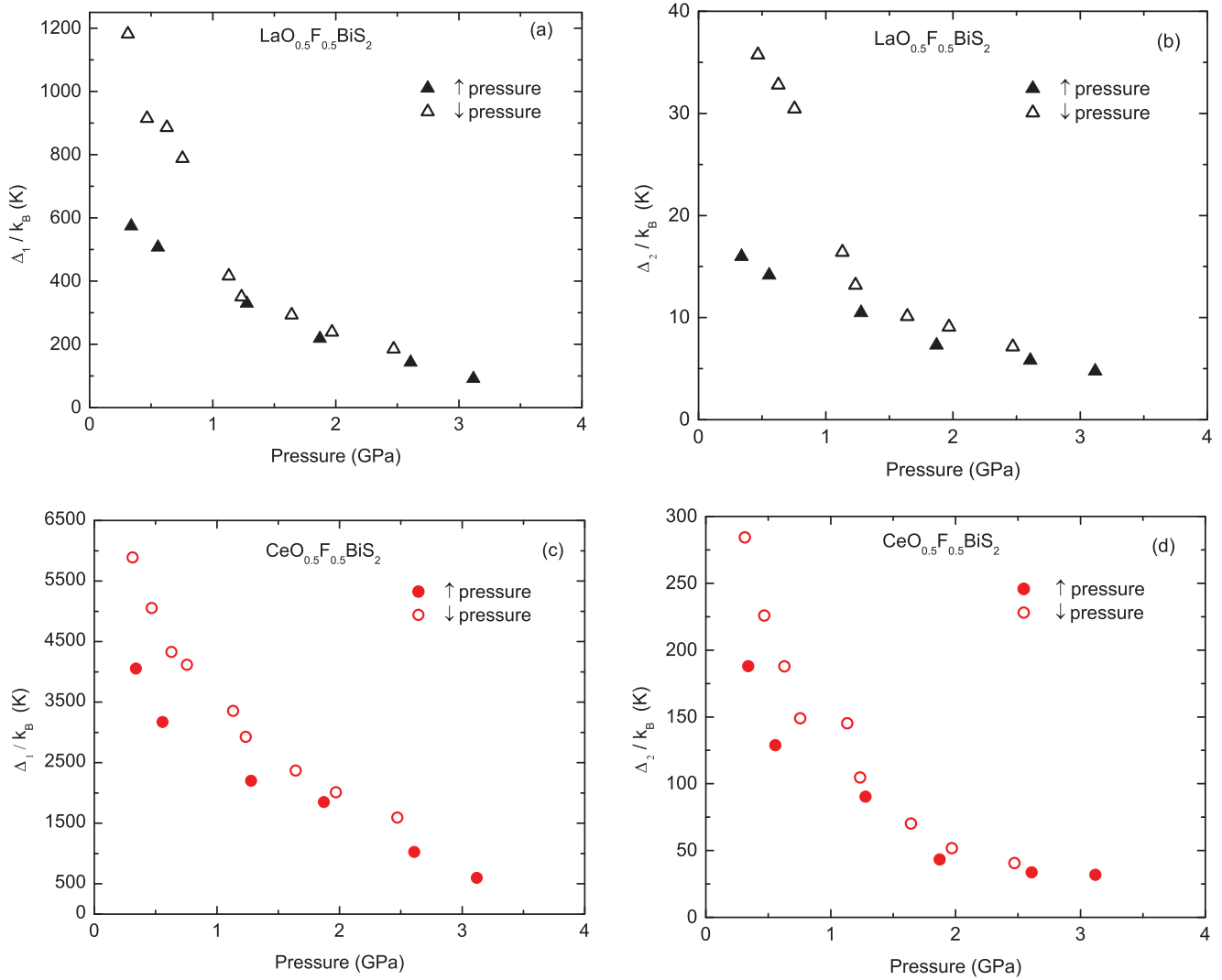


FIG. 6. (Color online) (a), (b) Energy gaps Δ_1 and Δ_2 plotted as a function of pressure for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$; (c), (d) Energy gaps Δ_1 and Δ_2 plotted as a function of pressure for $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$. Energy gaps were fitted with Eq. (1) using the data shown in Fig. 5. Filled (open) symbols were obtained upon increasing (decreasing) pressure cycles.

two energy gaps Δ_1 and Δ_2 , corresponding to the high and low temperature regions, respectively, could also be extracted.

The behavior of energy gaps Δ_1 and Δ_2 as a function of pressure for both $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ and $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ are shown in Fig. 6. The energy gaps decrease rapidly with pressure, similar to the behavior observed by Kotegawa *et al.*⁷ However, it is interesting to note that the values of the energy gaps for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ at atmospheric pressure shown in Fig. 6 are considerably larger than the values obtained by Kotegawa *et al.*⁷ The energy gaps Δ_1 and Δ_2 both exhibit hysteretic behavior below a critical pressure of ~ 1.3 GPa for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ and ~ 2 GPa for $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$; these critical pressures correlate with the pressures where the slope $d\log(\rho)/dP$ changes (at temperatures in the normal state right above T_c) in the $\log(\rho)$ vs P plots [Fig. 4] and also correlate with the transition pressures into the high T_c phase for both $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ and $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ [Fig. 3].

Specific heat $C(T)$ measurements at ambient pressure have recently been made on both the $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ and

$\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ compounds.¹² The samples in Ref. 12 and in the present study were from the same batch. In the case of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$, these $C(T)$ measurements suggest that the superconductivity observed at ~ 3 K for pressures less than ~ 0.5 GPa is a bulk phenomenon. In Fig. 5 of Ref. 12, there is a clear jump in $C(T)/T$ at $T_c = 2.93$ K. This value of T_c is close to the temperature where ρ vanishes in $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$. We expect, therefore, that the $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ sample in this study exhibits bulk superconductivity at lower pressures.

It is still unclear whether or not the higher T_c superconducting transitions at pressures above 0.5 GPa are associated with bulk superconductivity. The narrow widths of the superconducting transitions would seem to suggest that the superconductivity in this pressure range is a bulk phenomenon. However, the sharpness of the resistive transitions is also consistent with a filamentary zero resistance path through the sample with a narrow distribution of T_c values that could be due to small amounts of a superconducting phase, rather than bulk superconductivity. High pressure magnetization

measurements in a SQUID magnetometer were performed on several pieces of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ to determine the character of the 10 K superconducting phase by Taufour, Bud'ko, and Canfield.¹⁵ It was difficult to observe a diamagnetic signal against the large background from the pressure cell. This suggests possible inhomogeneity in the $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ sample.

In the case of $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$, however, there is no indication in the ambient pressure $C(T)$ measurements of bulk superconductivity.¹² The lack of a discernible jump in specific heat, however, could be due to sample inhomogeneity and/or the proximity of $T_c = 1.9$ K to the base temperature $T = 1.8$ K of the specific heat measurements and needs to be investigated further.

The rapid increase of T_c and broadening of the superconducting transition with pressure, as well as its reversibility with pressure for both compounds, suggest the existence of a gradual, pressure-induced transition between superconducting phases with a lower T_c at lower pressure and a higher T_c at higher pressure. The broadening of the superconducting transition feature in the transition region, ~ 1 GPa wide for both compounds, could be a consequence of the large slope of $T_c(P)$ in that pressure range [i.e., $\Delta T_c \simeq (dT_c(P)/dP)\Delta P$]. It might also be due to a spatial distribution of the two phases in the transition region. In this latter scenario, as the applied pressure is increased in the transition region, the amount of the high pressure phase grows at the expense of the low pressure phase, until the sample is completely transformed into the high pressure phase at the end of the transition region. The markedly similar features in the T_c versus pressure diagrams shown in Fig. 3 for the two compounds $\text{LnO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ ($\text{Ln} = \text{La}, \text{Ce}$) suggests that this behavior could be characteristic in general of the entire class of $\text{LnO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ materials.

One possible explanation for this behavior is that there is a distribution of pressures at which the transformation between the two phases takes place within the transition region. This distribution could be associated with some type of inhomogeneity (either electronic or atomic) in the samples. Experiments are currently in progress to search for a possible pressure-induced structural transition in these materials and to see whether the pressure-induced transition can be sharpened by improving the synthesis methods. The synthesis of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ under pressure with a T_c of 10.6 K suggests the possibility that the transformation pressure between the low and high pressure phases can be reduced to zero pressure by using a different synthesis route.¹⁰

IV. SUMMARY

We have observed a striking enhancement of superconductivity accompanying the suppression of semiconducting behavior with pressure in the $\text{LnO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ compounds ($\text{Ln} = \text{La}, \text{Ce}$) at critical pressures of ~ 1.1 GPa and ~ 2.0 GPa for $\text{Ln} = \text{La}$ and Ce , respectively. There is markedly similar behavior in the electrical resistivity measurements under applied pressure for these two BiS_2 -based superconductors $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ and $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$. Electrical resistivity measurements reveal that for both compounds, the suppression of their semiconducting behavior is hysteretic upon application of pressure. The semiconducting behavior of the electri-

cal resistivity is consistent with two energy gaps that are suppressed with pressure in a similar way. The pressure dependence of the electrical resistivity exhibits hysteresis below a critical pressure where there is a change in slope of $\log(\rho)$ vs P and where the maximum value of T_c is observed. Furthermore, for both compounds, we have discovered a continuous and reversible transient region between regions of low and high T_c , which is characterized by a broadening of the superconducting transition; however, the mechanism behind the broadening of the superconducting transitions between the lower and higher T_c regions is unclear. The broadening could be a simple consequence of the sensitive pressure dependence of T_c in this region, which, when coupled with even a modest pressure gradient, could result in broader measured superconducting transitions. Sample inhomogeneity might also be responsible for the distribution of transition pressures seen in the broadening region, and the possibility of pressure-induced structural phase transitions is currently being investigated with x-ray diffraction measurements under pressure. Given the striking similarity in behavior for these two BiS_2 -based superconductors, further electrical resistivity measurements under pressure on other compounds could point to characteristic behavior of BiS_2 -based superconductors in general.

In experiments currently underway we have observed the same qualitative behavior for the $\text{NdO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ and $\text{PrO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ compounds as were observed in the $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ and $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ compounds suggesting this is indeed a general phenomenon in the class of $\text{LnO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ compounds. Our results on the $\text{NdO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ compound may be compared to the recently reported study of $\text{NdO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ specimens prepared in a solid state reaction by Selvan *et al.*¹⁶ For the compounds with $\text{Ln} = \text{La}, \text{Ce}$, and Pr , there is a dramatic decrease in the electrical resistivity with pressure that reflects a continuous suppression of semiconducting behavior. Although the temperature coefficient of the electrical resistivity $d\rho/dT$ at the highest pressures is small for these $\text{Ln} = \text{La}, \text{Ce}$, and Pr compounds, the coefficient nevertheless remains negative ($d\rho/dT < 0$), so that we cannot definitely conclude that the metallic state has been achieved. We have, however, been able to reach a metallic state for $\text{Ln} = \text{Nd}$, indicated by a positive temperature coefficient of resistivity ($d\rho/dT > 0$), consistent with a semiconductor-metal transition. Experiments to pressures in excess of 3 GPa are currently underway to see if definitive metallic states (i.e., $d\rho/dT > 0$) can be attained for the $\text{Ln} = \text{La}, \text{Ce}$, and Pr compounds.

ACKNOWLEDGMENTS

High pressure research at the University of California, San Diego (UCSD) was supported by the National Nuclear Security Administration under the Stewardship Science Academic Alliance Program through the US Department of Energy (DOE) under Grant No. DE-NA0001841. Sample synthesis at UCSD was sponsored by the US Air Force Office of Scientific Research under MURI Grant No. FA9550-09-1-0603 ("Broad-based search for new and practical superconductors," involving the University of Maryland, Iowa State University, and the University of California, San Diego). Characterization of

samples at ambient pressure was supported by the US DOE Grant No. DE-FG02-04-ER46105. We would like to thank V. Taufour, S. L. Bud'ko, and P. C. Canfield of Iowa State

University for performing magnetization measurements under pressure on several $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ samples under the auspices of the above mentioned AFOSR MURI project.

*Corresponding author: mbmaple@ucsd.edu

- ¹Y. Mizuguchi, H. Fujihisa, Y. Gotoh, K. Suzuki, H. Usui, K. Kuroki, S. Demura, Y. Takano, H. Izawa, and O. Miura, *Phys. Rev. B* **86**, 220510(R) (2012).
- ²S. K. Singh, A. Kumar, B. Gahtori, S. Kirtan, G. Sharma, S. Patnaik, and V. P. S. Awana, *J. Am. Chem. Soc.* **134**, 16504 (2012).
- ³B. Li, Z. W. Xing, and G. Q. Huang, *Europhys. Lett.* **101**, 47002 (2013).
- ⁴R. Jha, A. Kumar, S. K. Singh, and V. P. S. Awana, *J. Sup. and Novel Mag.* **26**, 499 (2013).
- ⁵R. Jha, A. Kumar, S. K. Singh, and V. P. S. Awana, *J. Appl. Phys.* **113**, 056102 (2013).
- ⁶K. Deguchi, Y. Mizuguchi, S. Demura, H. Hara, T. Watanabe, S. J. Denholme, M. Fujioka, H. Okazaki, T. Ozaki, H. Takeya, T. Yamaguchi, O. Miura, and Y. Takano, *Europhys. Lett.* **101**, 17004 (2013).
- ⁷H. Kotegawa, Y. Tomita, H. Tou, H. Izawa, Y. Mizuguchi, O. Miura, S. Demura, K. Deguchi, and Y. Takano, *J. Phys. Soc. Jpn.* **81**, 103702 (2012).
- ⁸V. P. S. Awana, A. Kumar, R. Jha, S. Kumar, A. Pal, Shruti, J. Saha, and S. Patnaik, *Solid State Commun.* **157**, 21 (2013).
- ⁹S. Demura, Y. Mizuguchi, K. Deguchi, H. Okazaki, H. Hara, T. Watanabe, S. J. Denholme, M. Fujioka, T. Ozaki, H. Fujihisa, Y. Gotoh, O. Miura, T. Yamaguchi, H. Takeya, and Y. Takano, *J. Phys. Soc. Jpn.* **82**, 033708 (2013).
- ¹⁰Y. Mizuguchi, S. Demura, K. Deguchi, Y. Takano, H. Fujihisa, Y. Gotoh, H. Izawa, and O. Miura, *J. Phys. Soc. Jpn.* **81**, 114725 (2012).
- ¹¹J. Xing, S. Li, X. Ding, H. Yang, and H.-H. Wen, *Phys. Rev. B* **86**, 214518 (2012).
- ¹²D. Yazici, K. Huang, B. D. White, A. H. Chang, A. J. Friedman, and M. B. Maple, *Philos. Mag.* **93**, 673 (2012).
- ¹³D. Yazici, K. Huang, B. D. White, I. Jeon, V. W. Burnett, A. J. Friedman, I. K. Lum, M. Nallaiyan, S. Spagna, and M. B. Maple, *Phys. Rev. B* **87**, 174512 (2013).
- ¹⁴T. F. Smith, C. W. Chu, and M. B. Maple, *Cryogenics* **9**, 53 (1969).
- ¹⁵V. Taufour, S. L. Bud'ko, and P. C. Canfield (private communication).
- ¹⁶G. Kalai Selvan, M. Kanagaraj, S. Esakki Muthu, R. Jha, V. P. S. Awana, and S. Arumugam, *Phys. Status Solidi RRL* **7**, 510 (2013).