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

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Electrical resistivity measurements as a function of temperature between 1 K 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 K 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. This region is characterized by a broadening of the superconducting transition, in which $T_c$ and the transition width $\Delta T_c$ 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.

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I. INTRODUCTION

Superconductivity with a superconducting critical temperature $T_c = 8.6$ K has recently been reported in the layered compound $Bi_2O_3S_2$. Following this report, other $Bi_2S_2$-based superconductors including $LnO_{1-x}F_xBiS_2$ ($Ln =$ La, Ce, Pr, Nd, Yb) with a $T_c$ as high as 10 K have been synthesized and studied. 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. Most of the research on the layered $Bi_2S_2$ 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 K and 300 K and $T_c$ at various pressures up to $\sim$ 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.

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 K and 2.2 K, respectively. For both compounds, $T_c$ initially increases, reaches a maximum value of 10.1 K at $\sim$ 1 GPa for $LaO_{0.5}F_{0.5}BiS_2$ and 6.7 K at $\sim$ 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. This transient region is characterized by a rapid increase of $T_c$ and an increase of the superconducting transition width $\Delta T_c$, in which both $T_c$ and $\Delta T_c$ are reversible with increasing and decreasing pressure cycles. This occurs over a range in pressure from $\sim$ 0.5 GPa to 1.1 GPa for $LaO_{0.5}F_{0.5}BiS_2$ and from $\sim$ 0.5 GPa 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 (99.9%) 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,
FIG. 1: (Color online) (a) (b) Temperature dependence of electrical resistivity, \( \rho \), for LaO\(_{0.5}\)F\(_{0.5}\)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 LaO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) upon (c) increasing and (d) decreasing pressure. \( T_c \) increases from \( \sim 3 \) K to a maximum of \( \sim 10 \) K before gradually decreasing.

Measurements of \( \rho(T) \) under applied pressure were performed up to \( \sim 3 \) GPa in a clamped piston cylinder pressure cell between \( \sim 1 \) K and 300 K in a pumped \(^4\)He dewar. A 1:1 by volume mixture of \( n \)-pentane and isoamyl alcohol was used to provide a quasi-hydrostatic 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, \( \rho \), below 300 K for LaO\(_{0.5}\)F\(_{0.5}\)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 Fig. 1(a) and Fig. 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 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 $\rho$ is nearly 14 mΩ 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 Fig. 1(c) and Fig. 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 GPa 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 pres-
pressure region where \( T_c \) passes through a maximum of 10.1 K at \( \sim 1 \) 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 width \( \Delta T_c \) 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 \( \rho \) falls to 50% of its value at the temperature of the onset of superconductivity, \( T_{c_{\text{onset}}} \), with \( T_c \) determined as illustrated in Fig. 1(c). The temperature where the resistivity vanishes, \( T_0 \), was determined in a similar fashion as \( T_{c_{\text{onset}}} \) 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 CeO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) reveal remarkably similar behavior to the LaO\(_{0.5}\)F\(_{0.5}\)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, \( \rho \) is nearly 130 mΩ 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 CeO\(_{0.5}\)F\(_{0.5}\)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 Fig. 2(c) and Fig. 2(d). Similar to the evolution of \( T_c \) in LaO\(_{0.5}\)F\(_{0.5}\)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 (Fig. 2(c) and Fig. 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 \( \sim 2 \) GPa and then decreases gradually at higher pressures.

Figure 3 summarizes the results for the superconducting phase diagram, \( T_c(P) \), for both the LaO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) and CeO\(_{0.5}\)F\(_{0.5}\)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(a) shows \( T_c \) maxima for...
behavior of LaO$_{0.5}$F$_{0.5}$BiS$_2$ that decreases with pressure, the values of which are ∼ $T_c$ taken at pounds. In the case of LaO$_{0.5}$F$_{0.5}$BiS$_2$ and CeO$_{0.5}$F$_{0.5}$BiS$_2$, respectively. The break in slope occurs at a pressure near that at which $T_c$ reaches a maximum for both LaO$_{0.5}$F$_{0.5}$BiS$_2$ and CeO$_{0.5}$F$_{0.5}$BiS$_2$. 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.

The width of the superconducting transitions in the broadening region, represented by the vertical bars in Fig. 5 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 $\Delta T_c$ and $\Delta P$ through the slope of $T_c(P)$ in Fig. 3 so that $\Delta T_c \approx (dT_c(P)/dP) \Delta P$. Even though $\Delta P$ is small and constant for pressures measured as part of this study, $\Delta T_c$ can be large when $dT_c(P)/dP$ is large (i.e., in the pressure region where broadened transitions are observed). Rough estimates of $\Delta T_c$ were made using $\Delta P = 0.1$ GPa and slopes of 18 K/GPa and 11 K/GPa for LaO$_{0.5}$F$_{0.5}$BiS$_2$ and CeO$_{0.5}$F$_{0.5}$BiS$_2$, respectively. These calculations yield values of $\Delta T_c = 1.8$ K and 1.1 K for LaO$_{0.5}$F$_{0.5}$BiS$_2$ and CeO$_{0.5}$F$_{0.5}$BiS$_2$, respectively, which are of the correct order of magnitude. The size of the vertical bars characterizing $\Delta T_c$ also appear to qualitatively track with the local slope of $T_c(P)$ for most pressures in Fig. 3.

Kotegawa et al. previously reported the pressure dependence of $T_c$ for LaO$_{0.5}$F$_{0.5}$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

![Graph 1](image1.png)

**FIG. 4:** (Color online) Electrical resistivity, $\rho$, in the normal state just above the superconducting onset temperature, $T_c^{\text{onset}}$. Electrical resistivity values for CeO$_{0.5}$F$_{0.5}$BiS$_2$ were taken at $T = 7.6$ K, while $\rho$ values for LaO$_{0.5}$F$_{0.5}$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 LaO$_{0.5}$F$_{0.5}$BiS$_2$ and CeO$_{0.5}$F$_{0.5}$BiS$_2$, respectively. The break in slope occurs at a pressure near that at which $T_c$ reaches a maximum for both LaO$_{0.5}$F$_{0.5}$BiS$_2$ and CeO$_{0.5}$F$_{0.5}$BiS$_2$.

![Graph 2](image2.png)

**FIG. 5:** (Color online) log($\rho$) vs. $1/T$ up to 3.12 GPa for LaO$_{0.5}$F$_{0.5}$BiS$_2$. The solid lines represent linear fits of Eq. 1 from which the high and low temperature gaps $\Delta_1$ and $\Delta_2$, respectively, were determined.
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.\textsuperscript{2} suggests that synthesis of the LaO$_{0.5}$F$_{0.5}$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.\textsuperscript{3} there is a noticeable change in the magnitude of the suppression rate, dlog($\rho$)/dP, for both the LaO$_{0.5}$F$_{0.5}$BiS$_2$ and CeO$_{0.5}$F$_{0.5}$BiS$_2$ compounds. In the case of LaO$_{0.5}$F$_{0.5}$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 CeO$_{0.5}$F$_{0.5}$BiS$_2$, there is a strong suppression of resistivity up to ~1.8 GPa, followed by a weaker suppression at higher pressures. The $\rho(P)$ data for LaO$_{0.5}$F$_{0.5}$BiS$_2$ and CeO$_{0.5}$F$_{0.5}$BiS$_2$ were taken in the normal state at 11 K and 7.6 K, respectively. These temperatures occur just above the onset of the superconducting transition at $T_c^{\text{onset}}$. The dotted lines in Fig.\textsuperscript{3} 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.\textsuperscript{3} and the pressure where the suppression rate changes in the plot of log($\rho$) vs. $P$ in Fig.\textsuperscript{3}. For LaO$_{0.5}$F$_{0.5}$BiS$_2$, this “critical pressure” occurs at ~1.2 GPa, while for CeO$_{0.5}$F$_{0.5}$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.\cite{12} on the LaO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) compound synthesized under high pressure. They observed that the resistivity could be described over two distinct regions by the relation

\[
\rho(T) = \rho_0 e^{\Delta/2k_B T}
\]

where \( \rho_0 \) is a constant and \( \Delta \) 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 \( \Delta_1/k_B \approx 140 \) K and \( \Delta_2/k_B \approx 1.86 \) K, respectively. Both energy gaps \( \Delta_1 \) and \( \Delta_2 \) were found to decrease with pressure. In this study, we have also determined values of the energy gaps \( \Delta_1 \) and \( \Delta_2 \) 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 LaO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) upon increasing pressure. From similar plots for LaO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) upon decreasing pressure as well as for CeO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) upon increasing and decreasing pressure, the two energy gaps \( \Delta_1 \) and \( \Delta_2 \), corresponding to the high and low temperature regions, respectively, could also be extracted.

The behavior of energy gaps \( \Delta_1 \) and \( \Delta_2 \) as a function of pressure for both LaO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) and CeO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) are shown in Fig. 6. The energy gaps decrease rapidly with pressure, similar to the behavior observed by Kotegawa et al.\cite{12} However, it is interesting to note that the values of the energy gaps for LaO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) at atmospheric pressure shown in Fig. 6 are considerably larger than the values obtained by Kotegawa et al.\cite{12}

The energy gaps \( \Delta_1 \) and \( \Delta_2 \) both exhibit hysteretic behavior below a critical pressure of \( \sim 1.3 \) GPa for LaO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) and \( \sim 2 \) GPa for CeO\(_{0.5}\)F\(_{0.5}\)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 LaO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) and CeO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) (Fig. 4).

Specific heat \( C(T) \) measurements at ambient pressure have recently been made on both the LaO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) and CeO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) compounds.\cite{12} The samples in Ref. 12 and in the present study were from the same batch. In the case of LaO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\), these \( C(T) \) measurements suggest that the superconductivity observed at \( \sim 3 \) K for pressures less than \( \sim 0.5 \) 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 \( \rho \) vanishes in LaO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\). We expect, therefore, that the LaO\(_{0.5}\)F\(_{0.5}\)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 LaO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) to determine the character of the 10 K superconducting phase by Taufour, Bud’ko and Canfield.\cite{12} It was difficult to observe a diamagnetic signal against the large background from the pressure cell. This suggests possible inhomogeneity in the LaO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) sample.

In the case of CeO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\), however, there is no indication in the ambient pressure \( C(T) \) measurements of bulk superconductivity.\cite{12} The lack of a discernable 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, \( \sim 1 \) 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. 5 for the two compounds \( LnO_{1-x}F_xBiS_2 \) (\( Ln = La, \ Ce \)) suggests that this behavior could be characteristic in general of the entire class of \( LnO_{1-x}F_xBiS_2 \) 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 LaO$_{0.5}$F$_{0.5}$BiS$_2$ under pressure with a $T_c$ of $\sim 10$ 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.\(^1\)

**IV. SUMMARY**

We have observed a striking enhancement of superconductivity accompanying the suppression of semiconducting behavior with pressure in the $LnO_{0.5}F_{0.5}BiS_2$ compounds ($Ln = La, Ce$) at critical pressures of $\sim 1.1$ GPa and $\sim 2.0$ GPa for $Ln = La$ and Ce, respectively. There is markedly similar behavior in the electrical resistivity measurements under applied pressure for these two BiS$_2$-based superconductors LaO$_{0.5}$F$_{0.5}$BiS$_2$ and CeO$_{0.5}$F$_{0.5}$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 electrical 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 NdO$_{0.5}$F$_{0.5}$BiS$_2$ and PrO$_{0.5}$F$_{0.5}$BiS$_2$ compounds as were observed in the the LaO$_{0.5}$F$_{0.5}$BiS$_2$ and CeO$_{0.5}$F$_{0.5}$BiS$_2$ compounds suggesting this is indeed a general phenomenon in the class of LnO$_{0.5}$F$_{0.5}$BiS$_2$ compounds. Our results on the NdO$_{0.5}$F$_{0.5}$BiS$_2$ compound may be compared to the recently reported study of NdO$_{0.5}$F$_{0.5}$BiS$_2$ specimens prepared in a solid state reaction by Selvan et al.\(^2\) For the compounds with $Ln = La$, Ce and Pr, there is a dramatic decrease in the electrical resistivity with pressure that reflects a continuous suppression of superconducting behavior. Although the temperature coefficient of the electrical resistivity, $dp/dT$, at the highest pressures is small for these $Ln = La$, Ce and Pr compounds, the coefficient nevertheless remains negative ($dp/dT < 0$), so that we cannot definitely conclude that the metallic state has been achieved. We have, however, been able to reach a metallic state for $Ln = Nd$, indicated by a positive temperature coefficient of resistivity ($dp/dT > 0$), consistent with a semiconductor-metal transition. Experiments to pressures in excess of 3 GPa are currently under way to see if definitive metallic states (i.e., $dp/dT > 0$) can be attained for the $Ln = La$, Ce, and Pr compounds.

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