Disorder Driven Metal-Insulator Transition in $\mathbf{BaPb_{1-x}Bi_xO_3}$ and Inference of Disorder-Free Critical Temperature

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We performed point-contact spectroscopy tunneling measurements on single crystal $\mathrm{BaPb_{1-x}Bi_xO_3}$ for $0 \leq x \leq 0.28$ at temperatures $T = 2$–40 K and find a suppression in the density of states at low bias voltages that is characteristic of disordered metals. Both the correlation gap and the zero-temperature conductivity are zero at a critical concentration $x_c = 0.30$. Not only does this suggests that a disorder driven metal-insulator transition occurs before the onset of the charge disproportionated charge density wave insulator, but we also explore whether a scaling theory is applicable. In addition, we estimate the disorder-free critical temperature and compare these results to $\mathrm{Ba_{1-x}K_xBiO_3}$.

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The bismuthate superconductors (doped $\mathrm{BaBiO_3}$) were among the first class of oxide superconductors to be discovered [1,2]. They exhibit moderately high superconducting transition temperatures [up to ∼12 K in $\mathrm{BaPb_{1-x}Bi_xO_3}$ (BPBO) and ∼30 K in $\mathrm{BaK_xBi_{1-x}O_3}$ (BKBO)], and they are another example of a high T_c superconducting phase adjacent to a competing ordered phase, only in this case the ordered phase is in the charge sector [3,4]. They were highly studied in the era before the discovery of the cuprate superconductors.

Still, despite this considerable effort, neither the electronic structure of these materials nor the ingredients of their superconductivity could be satisfactorily treated theoretically [5–7]. Simple valance arguments suggest that the parent compound $\mathrm{BaBiO_3}$ should be a half-filled band metal with Bi in a 4+ valence state, whereas in fact it is an insulator due to charge disproportionation (e.g., $\mathrm{Bi^{4+} \rightarrow Bi^{3+} + Bi^{5+}}$) lending to a so-called charge disproportionated charge density wave (CD-CDW), which is a distinct form of CDW not associated with Fermi surface nesting. One can also think of the CD-CDW as arising from a negative U on the Bi sites. Traditional density functional electronic structure calculations were not able to account for this CD-CDW state, and the most up to date calculations of the electron-phonon (e-ph) interaction parameter λ yield values that are too small to account for the observed high transition temperatures [5].

Recently, the theoretical situation has greatly improved. Franchini *et al.* first showed that the insulating state (as well as the structure and lattice constants) of $\mathrm{BaBiO_3}$ could be understood within density functional theory if the HSE functional was used [8,9]. This functional is computationally more complex but incorporates better the Coulomb correlations present in the bismuthates. Using this approach, Yin, Kutepov, and Kotliar showed that λ in the bismuthates was “dynamically” enhanced and that these larger values could account for the observed T_c's. In their work, to calculate T_c, these authors used the strong-coupled McMillan formulation of the Eliashburg theory with calculated values of λ and the renormalized Coulomb interaction parameter μ^* [10].

In this Letter, we show that the effects of disorder (localization) are another essential factor in understanding these materials that has not been appreciated previously. Specifically, we show that in BPBO there is a disorder-induced metal-insulator transition (MIT) at a composition $x_c < x_{\mathrm{CDW}}$ where x_{CDW} is the critical concentration at which the CD-CDW state forms, or, more precisely, there is an opening of a gap in the optical spectrum at $x = 0.35$ that is generally presumed to reflect charge disproportionation, at least locally. For $x < x_c$ we also observe a reduction in the tunneling density of states (DOS) at the Fermi level that is expected due to electron-electron interactions in the presence of disorder. When such disorder effects are present, one also expects a reduction of T_c due to a disorder-enhanced μ^*, as first noted by Fukuyama, Ebisawa, and Maekawa [11].

Building on this fact, and using the most complete theory of the effects of disorder on T_c, we show that it is possible to back out an estimate of the disorder-free transition temperature T_{c0} from our data. The result is that in the case of BPBO the maximum inferred T_{c0} is around a factor of 2 higher than the experimental value at optimal doping.

The existence of a MIT is demonstrated in Fig. 1 where the zero-temperature conductivity σ_0 is plotted as a function of composition. The conductivity decreases linearly to the critical value $x_c = 0.30$. The blue lines are obtained from the four-point resistivity measurement shown in Fig. 2 of Ref. [12], where a linear extrapolation is made using points prior to the onset of T_c. The variation is due to geometrical factors from four to five resistivity measurements per doping concentration. The red diamonds correspond to σ_0 for the exact samples used in the tunneling measurements discussed below. Note that in the literature the best

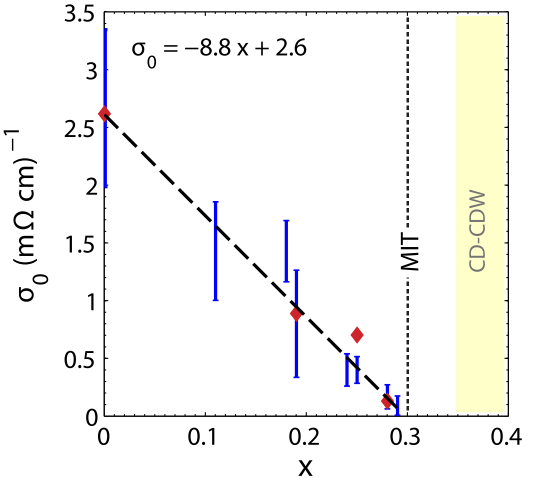

FIG. 1 (color online). Zero temperature conductivity vs concentration derived from resistivity measurements. Blue lines are from four to five crystals per x. Red diamonds correspond to samples used in the tunneling experiments. Dashed line is a linear fit to these data points. Note that the maximum T_c occurs at $x = 0.25$ on the metal side of the MIT.

estimates of the concentration for the onset of the CD-CDW state is $x_{\mathrm{CDW}} = 0.35$ [3]. (See yellow region in the figure.)

Examples of our tunneling data are shown in Figs. 2(a) and 2(b). The data were obtained using point-contact spectroscopy (PCS) measurements on single crystals of $\mathrm{BaPb}_{1-x}\mathrm{Bi}_x\mathrm{O}_3$ (BPBO) with doping concentrations $x = 0$, 0.19, 0.25, and 0.28, and grown in a method described in Ref. [12]. Measurements were performed from temperatures ranging from 2–40 K. The junctions were prepared by cleaving the sample in air and then at room temperature, bringing the sample in contact with a 0.5 mm diameter aluminum tip. The apparatus was then inserted into a flow cryostat for measurements. For the differential conductance measurements, G, the polarity of the tip was positive voltage and current, while the sample was negative. As shown in Fig. 2(a), for $x = 0.25$, superconducting DOS were observed that are consistent with those reported in the past by several researchers [13–16]. A fit of G normalized at 5 mV at temperature $T = 2.6$ K with Blonder-Tinkham-Klapwijk (BTK) theory yields a gap $\Delta = 1.55$ meV, smearing parameter $\Gamma = 0.54$ meV and barrier parameter $Z = 20$ [17–19]. We are not insisting on the precision of the fits, only that we confirm that which is evident in Fig. 2(a) itself, i.e., that we are in the tunneling regime. In the inset of Fig. 2(a), G measured out to high voltage is shown. While the asymmetry was only noted for optimal doping in the literature [20], this temperature independent linear asymmetric background is present in all concentrations, including $x = 0$ (See Supplemental Material [21].

However, in Fig. 2(b), we focus on the DOS above T_c, which is a region where little attention has been given. A cusp is observed in G, as shown, for example, in the inset of Fig. 2(b), which shows the tunneling DOS at low bias voltages for $x = 0$ (i.e., BPO, which is not a superconductor). Similar cusps are seen for all concentrations ($x \leq 0.28$) including those that are superconducting. To our knowledge, this cusp has not been noted previously, where historically attention has been focused on the unexplained asymmetric v-shaped tunneling DOS at higher voltages [20].

On the other hand, the cusp we report is similar to that seen in amorphous Nb-Si alloys [22], which is one of the classic cases of a disorder driven (localization) MIT. In Fig. 2(b) the data have been normalized to G at 25 mV, which we take as a measure of the background DOS free of disorder effects. There is some arbitrariness in this choice due to the unexplained linear background at high bias voltages universally seen in bismuth tunneling data. On the other hand, examination of the inset in the figure indicates that the zero-bias anomaly of interest to us merges into the linear background in the vicinity of 25 mV. The physical assumption here is that the linear background is a higher energy phenomenon that crosses over to the well-known low-energy reduction of the density of states as voltage goes to zero due to enhanced Coulomb interactions in disordered materials.

The theory of the reduction of the DOS, $N(E)$, due to disorder-enhanced Coulomb interactions is well established. In three dimensions, it predicts that $N(E) = N(0)[1 + (E/\Delta)^{1/2}]$, where $N(E)$ is the DOS at zero temperature and Δ is the correlation gap [23]. As shown in Fig. 2(b), our data follow this energy dependence very well, where we plot the normalized tunneling DOS vs the square root of the bias voltage for various temperatures. From the fit to the data (dashed line), we determine both the correlation gap Δ (inverse slope) and the zero-temperature reduction in the DOS at zero-bias $N(0)$ (zero voltage intercept). Additionally, the temperature dependence of G/G (25 mV) when extrapolated to $T = 0$, matches quite closely to the zero voltage intercept.

A similar procedure is performed for the other concentrations, and the results are shown by the filled shapes in Fig. 2(c), again normalizing G by its value at 25 meV. Results when normalizing at 50 and 75 mV are depicted in the figure with nonfilled and hatched shapes, respectively. Some of these circles have been displaced horizontally for visual clarity. As seen in Fig. 2(c), if we normalize G at these higher voltages, $N(0)$ is substantially reduced as one fully expects. On the other hand, delta is affected only slightly, particularly at the interesting composition $x = 0.25$, where T_c is maximum. As noted above, we believe that the changes here represent the affect of the different physics at high energy, and in the remainder of this Letter we will use the data normalized at 25 meV. As the conductance is asymmetric, results differ between positive and negative bias voltages. The differences are not large, however, and for clarity of presentation we show only the data for positive bias. The circles represent Δ, and the squares represent $N(0)$. As is evident in the figure, Δ nicely

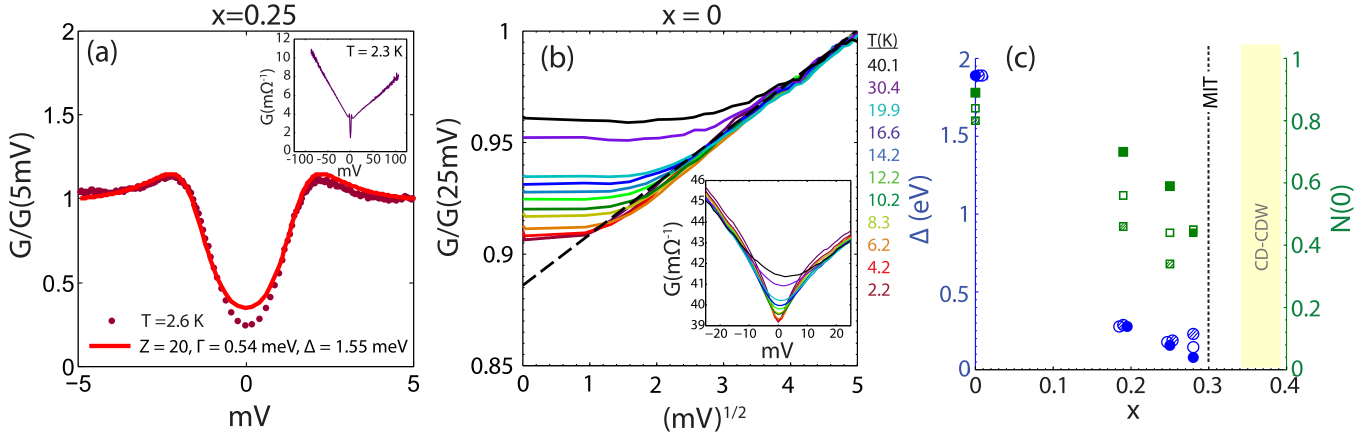

FIG. 2 (color online). (a) BTK fit of differential conductance normalized at 5 mV taken at $T = 2.6$ K. Inset shows the differential conductance taken out to high bias voltage. (b) Differential conductance normalized at 25 mV as a function of the square root of positive bias voltage for $x = 0$ at various temperatures. Inset shows raw data. (c) Correlation gap Δ (blue circles), and zero temperature at zero-voltage DOS N(0) (green squares) vs concentration x. Filled, nonfilled, and hatched shapes correspond to results when G is normalized at 25, 50, and 75 mV, respectively. Some blue circles are displaced horizontally around the filled circles for visual clarity. Results using positive bias voltage are shown.

extrapolates to zero at $x_c = 0.30$, which also occurs when using negative bias-voltage results.

Having established the existence of a MIT due to disorder, it is of interest to compare our results with McMillan's scaling theory [24] of such transitions that was developed to account for the disorder-driven MIT seen in $\mathrm{Nb}_x\mathrm{Si}_x$ [22]. The scaling theory involves two critical exponents $\nu \sim 1$ and $1 < \eta < 3$. In terms of these exponents, the theory predicts for $E < \Delta$ that $\sigma_0 \sim (x - x_c)^\nu$, $N(E) = N(0)[1 + (E/\Delta)^{1/2}]$, $\Delta = (x - x_c)^{\nu\eta}$ and $N(0) \sim (x - x_c)^{\nu(3-\eta)}$. Our transport and tunneling DOS data are nicely consistent with the first two predictions of the theory and yield a value $\eta = 1$. The fits for Δ and $N(0)$ as functions of x are not consistent. The first yields $\eta = 1.7$ and the second, $\eta = 2.7$.

Granted more data points would yield more accurate results. Also, as noted above, some uncertainty is associated with the normalization procedure in the tunneling data. We should also note that the scaling theory is only valid around the critical region, whereas we are including points at $x = 0$, which is relatively far from x_c. And, as pointed out by Lee and Ramakrishnan [25,26], McMillan's scaling theory may not be complete. Last but not least, the theory does not consider what would happen when the MIT is very near a CD-CDW transition. In short, we are entering unexplored territory.

Let us now turn to the issue of the reduction of T_c due to disorder. From the work of Belitz [27], we have a McMillan-like equation for T_c, valid for strong coupling and relatively strong disorder:

$$T_c = \frac{\Theta_D}{1.45} \exp\left[\frac{-1.04(1 + \tilde{\lambda} + Y')}{\tilde{\lambda} - \tilde{\mu}^*[1 + 0.62\tilde{\lambda}/(1 + Y')]}\right]. \quad (1)$$

We use the prefactor shown rather than $\omega_{\log}/1.2$, as not enough information is known to determine $\omega_{\log}$.

Conveniently, the disorder is parametrized by the fractional reduction of the DOS at the Fermi energy

$$Y' = N_F/N(\bar{\omega}) - 1, \quad (2)$$

where $N(\bar{\omega})$ is the DOS evaluated at a characteristic phonon frequency, and N_F is the clean normal-metal DOS at the Fermi level. For simplicity, we take $\bar{\omega} = 0$.

Y' enters the equation for the reduction of T_c both explicitly as shown in the equation and implicitly through the disorder-dependent e-ph coupling $\tilde{\lambda}(Y') > \lambda$ and the disorder-dependent Coulomb pseudopotential $\tilde{\mu}^*(Y') > \mu^*$.

In the theory of Belitz, both $\tilde{\mu}^*$ and $\tilde{\lambda}$ also depend on the ratio between the Thomas Fermi screening wave number and the Fermi wave number, $x = 2k_F/k_{TF}$. We estimate these wave numbers using simple band relations $k_F = (3\pi^2 n)^{1/3}$ and $k_{TF} = (6\pi n e^2/\epsilon_\infty E_F)^{1/2}$, where $\epsilon_\infty = 1$. Experimental results of the Debye temperature [28], Fermi energy [29], and carrier density [30] were used where there is a nice summary of these parameters for various concentrations shown in Table 1 of Ref. [31]. The renormalized Coulomb interaction μ^* with no disorder is also estimated using the Morel-Anderson equation, $\mu^* = \mu/[1 + \mu \ln(E_F/k_B\Theta_D)]$ with $\mu = (1/2x^2)\ln(1 + x^2)$ [32]. This procedure produces the value $\mu^* = 0.14$.

Using this theory, for an assumed value of T_{c0} (or, equivalently, λ) and the calculated value of μ^*, we can graphically depict the dependence of T_c on the disorder parameter Y' for BPBO, as shown in the inset of Fig. 3 for $x = 0.25$. A family of curves exist for various starting points of T_{c0}. As the disorder parameter Y' increases, T_c is suppressed. We are able to triangulate which curve in the

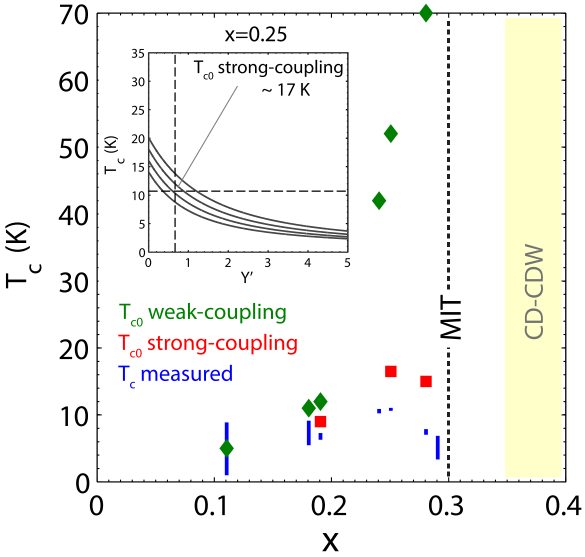

FIG. 3 (color online). Blue lines are the measured T_c for four to five samples derived from dH_{c2}/dT vs T. The inferred T_{c0} with no disorder is shown in the strong-coupling (squares) and weak-coupling regime (diamonds). Inset shows T_c decreasing with the disorder parameter Y' for $x = 0.25$ for the strong-coupling theory. From the intersection of the measured T_c and Y' of the material, T_{c0} where $Y' = 0$ can be backtracked.

figure is relevant to our material, as we measured T_c (horizontal dashed line), and we determined $N(0)$ from our measurements. Hence, we know $Y' = N_F/N(\bar{\omega}) - 1 \approx 1/N(0) - 1$ (vertical dashed line). The intersection of these two lines determines the curve relevant to our sample. Tracing back the curve to $Y' = 0$ determines the critical temperature with no disorder, $T_{c0} \approx 17$ K for this concentration.

With this procedure, the estimated T_{c0}'s for $x = 0.19$, 0.25, and 0.28 are shown as red squares in Fig. 3. The blue lines show the measured T_c's. Uncertainties in the input parameters (Θ_D, E_F, n, T_c) change T_{c0} at most a few degrees and the uncertainty in Y' is hard to assess in the absence of an understanding of the linear background. However, the trends observed as x goes to x_c should not be affected, although given the uncertainties, it is unclear whether the maximum in T_{c0} is real or not

In Fig. 4 we show the corresponding disorder-dependent e-ph coupling $\tilde{\lambda}$ (circles) and the disorder-dependent Coulomb pseudopotential $\tilde{\mu}$ (squares) as a function of doping in the strong-coupling regime. The data suggest a divergence of these quantities as the disorder induced metal-insulator transition is approached. This possibility raises interesting theoretical questions.

In estimating T_{c0}, it is instructive to consider the original weak coupling, weak disorder limit of the theory [11]. First, the determination of the material parameters in this limit is simpler and free of the uncertainties in the determination of Y' noted above. Second, it permits a comparison of the reduction in T_c found here for BPBO

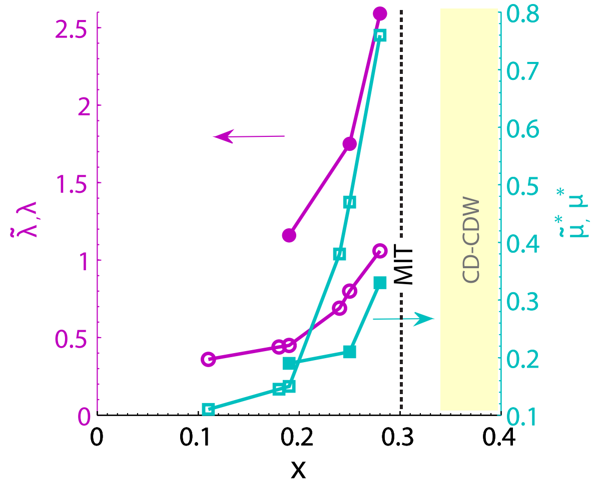

FIG. 4 (color online). The e-ph coupling strength in the strong-coupling (filled circle) $\tilde{\lambda}$, and weak-coupling regime (open circle) λ, vs doping x. Additionally shown is the Coulomb pseudopotential in the strong-coupling (filled square) $\tilde{\mu}^*$ and weak-coupling regime (open square) μ^*, vs x.

with that of BKBO. In this theory, the only parameter necessary to characterize the disorder is λ_{loc}, which is related to the diffusion constant, and in the dirty limit is related to upper-critical field measurements dH_{c2}/dT $(\lambda_{\text{loc}} = \hbar/2\pi E_F \tau = \hbar/2\pi(1/2m^* v_F^2)\tau = \hbar/3\pi m^* D \approx (m/3m^*)[(dH_{c2}/dT)/(30\ \text{kOe/K})]$. Using upper-critical field measurements, we can again produce similar curves as in Fig. 3. The results are shown as diamonds in Fig. 3 and the corresponding e-ph coupling strength and renormalized Coulomb interaction is shown in Fig. 4. The value of T_{c0} for $x = 0.2$ is slightly larger than the value obtained with the Belitz theory. For $x = 0.25$, $T_{c0} = 70$ K. Of course, as expected, at some point the theory of weak disorder and weak coupling breaks down with x, as indeed $T_c = 70$ K is quite high. In any event, the reasonable agreement at lower values of x supports the results found with the Belitz theory, mitigating any concerns with parameter determination in that case.

Performing a similar analysis on the optimally doped BKBO, we find that the critical temperature does not change significantly. For the analysis, we used literature values [33–35] and took $E_F = 1$ eV and $\mu^* = 0.1$. While the measured critical temperature is $T_c = 27$ K, the disorder-free $T_{c0} = 32$ K in the weak-coupling and weak-disorder regime. This shows that BKBO is relatively unaffected by disorder unlike BPBO.

The physical origin of the disorder in BPBO is not known. Two possibilities of the disorder are likely structural effects in concert with the chemical substitution of Bi in BPBO and/or the stripe-like nanoscale structural phase separation recently found [36]. The implications of these results in understanding the superconductor-insulator transition with phase fluctuations vs amplitude effects is being investigated.

In summary, we performed PCS measurements on BPBO at various temperatures and concentrations. In addition to corroborating results of the superconducting gaps and normal state linear background, we find a disorder driven MIT. The square root dependence of the differential conductance vs voltage is a classic signature of disorder. In addition, both the zero-temperature conductivity and correlation gap disappear around $x_c = 0.30$ before the onset of the CD-CDW. We suggest that a scaling theory might be applied to BPBO. Finally, we estimated the disorder-free critical temperature in BPBO and find that disorder affects the T_c of this material much more than in BKBO. Our results reconcile the differences seen in the shape of the superconducting dome, as well as T_c values, between BPBO and BKBO and provides a general phase diagram of this family of superconductors.

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