Cooling a polaronic liquid: Phase mixture and pseudogap-like spectra in superconducting $Ba_{1-x}K_xBiO_3$

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Many complex electronic systems exhibit so-called pseudogaps, which are poorly-understood suppression of low-energy spectral intensity in the absence of an obvious gap-inducing symmetry. Here we investigate the superconductor $Ba_{1-x}K_xBiO_3$ near optimal doping, where unconventional transport behavior and evidence of pseudogap(s) have been observed above the superconducting transition temperature T_c, and near an insulating phase with long-range lattice distortions. Angle-resolved photoemission spectroscopy (ARPES) reveals a dispersive band with vanishing quasiparticle weight and "tails" of deep-energy intensity that strongly decay approaching the Fermi level. Upon cooling below a transition temperature $T_p > T_c$, which correlates with a change in the slope of the resistivity vs. temperature, a partial transfer of spectral weight near E_F into the deep-binding energy tails is found to result from metal-insulator phase separation. Combined with simulations and Raman scattering, our results signal that insulating islands of ordered bipolarons precipitate out of a disordered polaronic liquid and provide evidence that this process is regulated by a crossover in the electronic mean free path.

Pseudogaps represent a departure from the expectations of standard band theory and the Fermi liquid theory of electronic excitations, which together serve as a successful starting point for understanding many condensed matter systems. They could potentially originate from any ways in which the conventional theories might break down, e.g., due to disorder, fluctuations, strong interactions, and/or strong correlations. But it is also conceivable that some observed pseudogaps might be less mysterious than they first seem, in the sense that they are rooted a "hidden" order

that, once revealed, could straightforwardly explain the opening of a gap.

Pseudogaps are often observed in strongly correlated transition metal systems where the charge, spin, orbital, and lattice degrees of freedom can intertwine, leading to the emergence of exotic and poorly understood phases. These include ordered insulator or "bad metal" phases near half-filling (e.g., Mott, charge density wave, and spin density wave orders), metal-insulator transitions, superconductivity, anomalous transport behaviors (e.g., "strange metal" behavior and colossal magnetoresistance), intrinsic disorder and phase separation/fluctuation. Examples of such phenomena are found in diverse materials, including the cuprates[1], manganites[2], transition metal dichalcogenides[3], iron-based superconductors[4], and rare earth nickelates[5].

In perovskite bismuth oxides such as $Ba_{1-x}K_xBiO_3$ (BKBO), a complex phenomenology similar to that of transition metal oxides emerges out of a very different setting. Here, short-range Coulomb and spin interactions can largely be neglected[6], but short-range electron-lattice interactions (polarons) play a crucial role, offering an opportunity to examine the signatures and origins of many-body phenomena from a new perspective. The phase diagram of BKBO is sketched in Fig. 1**a**. The insulating phase at zero doping ($x = 0$, half filling) is tied to a static long-range structural distortion. Here, alternating BiO_6 octahedra collapse in a three-dimensional breathing distortion, as illustrated schematically in the overlay of the phase diagram. Several studies have shown that the parent ground state is bond disproportionated, meaning that hole pairs are trapped in combinations of the O $2p$ orbitals in the collapsed octahedra, opening a gap in the predominantly oxygen-derived conduction band[6–10]. The localized charge pairs due to coupling to the

lattice distortion may be regarded as a frozen lattice of bipolarons. This polaronic view of the parent compound's ground state has been widely adopted in theoretical approaches to understanding the perovskite bismuth oxides[11–14].

BKBO transitions to a metal as a function of doping and/or temperature, and even becomes superconducting up to as high as 34 K in bulk[15]. Electrical transport evolves rapidly and dramatically as a function of doping across the superconducting region of the phase diagram. Measurements on single crystals by Nagata *et al.*[16] showed that at $x = 0.34$, resistivity rises with decreasing temperature down to about 75 K, where it saturates before T_c is reached. Although the high-T behavior of the resistivity at this doping resembles an insulator, our ARPES results will show that the slope change or "elbow" in (T) above T_c should be viewed as a bad-to-better metal transition. At $x = 0.39$ — close to what is generally cited as optimal doping[17] — (T) is nearly linear above T_c, with a weak elbow centered roughly around 140 K. Higher doped samples exhibit a more conventional, upward-curving (T).

The unusual transport above T_c in under-/optimally-doped superconducting samples appears to coincide with pseudogap-like spectral features. Optical conductivity studies of BKBO noted a suppression of the low-energy spectral weight at room temperature[18,19]. Similar spectra were found in an analogous region of the phase diagram of the closely related superconducting compound $BaPb_{1-x}Bi_xO_3$ (BPBO)[20]. Separately, angle-integrated photoemission measurements performed on superconducting BKBO observed an energetically sharper, temperature-dependent pseudogap-like suppression of near-E_F spectral intensity[21].

Some studies have interpreted the unusual transport and spectral properties of these materials as evidence of coexisting metallic and insulating phases[16,20,22]. Meanwhile a mixture of structural phases has been directly observed in superconducting BPBO compositions[23]. Based on transmission electron microscopy experiments, it appears that nanoscale regions of ordered distortions in BPBO tend to percolate into stripe-like formations[24]. This calls to mind predictions of 2D stacking "slices" of concentrated holes in BKBO[25] and strongly suggests that phase mixing is intrinsic to these materials in certain doping ranges. Overall, however, the ubiquity of structural phase mixing in superconducting bismuth oxides and its relationship to electronic structure and transport properties has remained unclear.

Here we use ARPES and Raman measurements to investigate the issues of possible pseudogaps and phase separation underlying BKBO's unusual transport characteristics. The ARPES experiments were performed *in situ* on freshly-grown thin films of BKBO, allowing us to overcome longstanding sample and surface quality issues associated with single crystals that had prevented successful ARPES measurements up to now. Figure 1**b** introduces typical resistance-vs.-temperature curves, $R(T)$, of our films grown by pulsed laser deposition (PLD) from ablation targets with $x = 0.34$ and $x = 0.38$. The curves are normalized to the resistance at 300 K. Aside from the lower superconducting transition temperatures in the films ($T_c = 22$ K) and slightly shifted temperatures of the elbow features relative to bulk BKBO, the $R(T)$ characteristics agree well with measurements of single crystals found in the literature[16]. We will later spectroscopically correlate the resistivity elbow with a transition temperature, T_p, to metal-insulator phase separation, thus defining the "M+I" region of the phase diagram in Fig. 1**a**. In what follows, we focus on