The low-energy excitations of the lightly doped cuprates were studied by angle-resolved photoemission spectroscopy. A finite gap was measured over the entire Brillouin zone, including along the $d_{x^2-y^2}$ nodal line. This effect was observed to be generic to the normal states of numerous cuprates, including hole-doped La$_{2-x}$Sr$_x$CuO$_4$ and Ca$_{2-x}$Na$_x$CuO$_2$Cl$_2$ and electron-doped Nd$_{2-x}$Ce$_x$CuO$_4$. In all compounds, the gap appears to close with increasing carrier doping. We consider various scenarios to explain our results, including the possible effects of chemical disorder, electronic inhomogeneity, and a competing phase.

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The parent compounds of the cuprates are half-filled antiferromagnetic insulators whose Coulomb repulsion opens a large charge-transfer gap ($\sim 2$ eV). While accurately describing the single particle excitations of the undoped insulator remains a theoretical challenge, this problem becomes far more daunting upon the addition of even a small number of holes or electrons. The exotic properties exhibited by these underdoped cuprates have led to numerous inquiries and debates over the physics of the insulator-superconductor transition, the presence of competing phases, precursor superconductivity, and electronic phase separation. While popular theoretical models (i.e. $t-J$ or Hubbard models) predict the formation of metallic states even at infinitesimally small doping concentrations, antiferromagnetic Néel order has been experimentally found to persist up to finite doping levels. Moreover, the doping range in which low temperature insulating behavior is observed has been universally found in the cuprates to extend well past the disappearance of Néel order. This naturally raises the question of the respective roles played by order (i.e. Néel order or alternative competing orders) and disorder (chemical or electronic inhomogeneity), on the low lying electronic states derived from doping the parent insulator.

To date, angle-resolved photoemission spectroscopy (ARPES) has been the premier tool for the direct study of the electronic structure of the near-optimally doped cuprates. However, its contributions to our understanding of the lightly doped regime have been extremely limited. The main reason for this disparity is that the bismuth based cuprates, the archetypal materials for ARPES, are naturally grown within a limited range around optimal doping, and thus it becomes necessary to study other families in order to access lighter dopings. Because of the extreme dearth of ARPES data in the lightly doped regime, a serious gap exists in our experimental understanding of the doping evolution of the electronic structure. Unfortunately, this deficiency in knowledge occurs where the physics of the cuprates is generally acknowledged to be most complex, further complicating attempts at understanding the physics of high-temperature superconductivity. It has been very recently shown that upon the addition of even a small concentration of carriers to the parent insulator, finite spectral weight develops near the chemical potential, as expected for a compressible thermodynamic system. While consistent with the high temperature metallic behavior seen at low concentrations, this near-$E_F$ weight has serious conflicts with the low temperature insulating behavior observed by charge and thermal transport. It is therefore important to ask whether this near-$E_F$ weight is additionally gapped at low energies. An energy gap along the $d$-wave node has not yet been observed, as previous work in the pseudogap regime was restricted to higher dopings where the nodal states were found to be ungapped. The presence of a gap along the nodal direction will clearly demonstrate the effects of disorder or additional orders on the ostensibly $d$-wave-like low energy states.

Here we report an extensive ARPES study of various lightly doped cuprates, where we find an apparently finite excitation gap in the normal state over the entire Brillouin zone. This result is observed for a variety of compounds and carrier concentrations, including hole-doped Ca$_{2-x}$Na$_x$CuO$_2$Cl$_2$ ($x = 0.05, 0.10$), La$_{2-x}$Sr$_x$CuO$_4$ ($x = 0.01, 0.02$), and electron-doped Nd$_{2-x}$Ce$_x$CuO$_4$ ($x = 0.025, 0.04$). This study reports the lowest doping concentrations ever studied by ARPES for each of the respective compounds, including La$_{2-x}$Sr$_x$CuO$_4$ with $x \leq 0.02$, where Néel order persists. The widespread absence of un-
gapped excitations in this regime suggests that this behavior may be generic to the cuprate superconductors instead of being a material-specific phenomenon. We consider a number of scenarios, including the presence of disorder and electronic inhomogeneity, as well as a possible competing order.

ARPES measurements were performed at Beamline 5-4 of the Stanford Synchrotron Radiation Laboratory with both synchrotron radiation and a He discharge lamp in conjunction with a Scienta SES-200 electron analyzer operating in parallel angle detection mode. The typical energy and angular resolutions used for these measurements were between 10 to 14 meV and 0.3°, respectively. Even with an energy resolution of 14 meV, edge positions could be measured accurately and reproducibly to within 1 meV. The Fermi energy ($E_F$) was determined from a polycrystalline Au target in direct electrical contact with the sample. Single crystals of La$_{2-x}$Sr$_x$CuO$_4$ and Nd$_{2-x}$Ce$_x$CuO$_4$ were grown using the travelling-solvent floating zone method, while single crystals of Ca$_{2-x}$Na$_x$CuO$_2$Cl$_2$ were grown using a self-flux method. Samples were first aligned by Laue diffraction in situ, and cleaved and measured at a base temperature of 15 K at a pressure of better than 5×10$^{-11}$ torr.

As previously observed in La$_{2-x}$Sr$_x$CuO$_4$ and Bi$_2$Sr$_2$CaCu$_2$O$_{8+y}$, the first hole addition states emerge near ($\pi$,0), the top of the lower Hubbard band of the undoped parent insulator‡ (for a comprehensive overview, see Ref. 3). At relatively low concentrations, the locus of low-lying spectral weight is confined to a discontinuous arc. Outside this sector, a large pseudo-gapped region devoid of well-defined low energy excitations persists around (\pi,0). As an example, we show spectra from Ca$_{1.8}$Na$_{0.1}$CuO$_2$Cl$_2$ in Figure 1 whose electronic structure has been shown to be consistent with the behavior described above. A dispersive excitation branch can be observed along the (0,0)-(\pi,\pi) line in Figure 1b. In Figure 1c, all spectra have been collapsed together and there exists a clear shift of all leading edge midpoints away from the chemical potential which we call a leading edge gap (LEG). As mentioned above, the locus of low-lying excitations in this compound is confined to an arc-like segment spanning approximately ±20° measured radially from (0,0). The angular dependence of this gap, $\Delta_{\text{LEG}}$, shown in Figure 1c, exhibits weak anisotropy within this arc. However, it is difficult to ascertain whether this apparent anisotropy is intrinsic, or due to the loss of spectral weight and broader lineshapes away from the nodal line, as illustrated by the larger error bars.

Spectra from non-superconducting ($x = 0.05$) and underdoped ($x = 0.10$, $T_C = 13$ K; $x = 0.12$, $T_C = 22$ K) compositions of Ca$_{2-x}$Na$_x$CuO$_2$Cl$_2$ are shown at the bottom of Figure 1. While no well-defined peak is visible for $x = 0.05$, there exists a distinct edge structure with $\Delta_{\text{LEG}} = 7$ meV. This effect decreases with hole doping and appears to close by $x = 0.12$. To demonstrate that this effect is generic to all cuprates, we also present results from very lightly doped, non-superconducting La$_{2-x}$Sr$_x$CuO$_4$ and Nd$_{2-x}$Ce$_x$CuO$_4$ in Figure 2 summarizing our findings regarding this LEG. For La$_{2-x}$Sr$_x$CuO$_4$, the topology of low-lying excitations is qualitatively similar to Ca$_{2-x}$Na$_x$CuO$_2$Cl$_2$, and the spectra are likewise taken from the $d_{x^2-y^2}$ nodal line. At a doping concentration of $x = 0.01$, dispersive low-energy states are observed with a $\Delta_{\text{LEG}} = 9$ meV. However, by $x = 0.03$, this LEG has closed, to within our experimental resolution, and remains as such for higher concentrations, as studied in detail in Ref. 7 (which focuses on the metallic behavior for $x \geq 0.03$). In the case of lightly electron-doped Nd$_{2-x}$Ce$_x$CuO$_4$, the first electron addition states appear as small electron pockets near ($\pi$,0)\π, in contrast to the hole-doped cuprates. In this case, we have observed the gap along these electron pockets with $\Delta_{\text{LEG}} \sim 16$ meV for $x = 0.025$, while for $x = 0.04$, $\Delta_{\text{LEG}} \sim 8$ meV, and closes to nearly zero by $x = 0.08$; at higher concentrations ($x > 0.10$), the Fermi surface crosses over to a hole pocket centered at ($\pi$, $\pi$).

The measurement of a LEG is the canonical scheme by which excitation gaps have been typically determined by photoemission spectroscopy. It is difficult to ascertain the precise value of any excitation gap from the measurement of the gap without a priori knowledge of the
A single-particle spectral function, $A(k, \omega)$, making lineshape modelling potentially suspect. However, the LEG criterion has typically been successful in identifying the $d$-wave gap in the superconducting cuprates, charge density wave (CDW) gaps, and even small superconducting gaps in photoemission studies of conventional BCS materials such as $V_2$Si, Nb, and $Pb_{1.15}$. Furthermore, our observation of finite LEGs in a wide variety of lineshapes and compounds suggests that this effect is not a misidentification due to a peculiar lineshape profile. Nevertheless, we should note that it is not inconceivable that in particular special instances, an ungapped spectral function may possibly give rise to a finite LEG in the ARPES lineshape (e.g. Luttinger liquids). All results were confirmed by multiple measurements on different sample batches. We have also utilized the method of symmetrization where $I_{\text{sym}}(k, \omega) = I(k, \omega) + I(k, -\omega)$, which has been demonstrated to be an effective procedure for determining the presence of Fermi crossings. The results obtained from this method were qualitatively consistent with values obtained by taking the leading edge midpoints of the spectra.

Particular care was taken to avoid any electrostatic charging, a possible consideration due to the low-temperature insulating tendencies of these lightly doped samples. No change in $\Delta_{\text{LEG}}$ was observed when the photon flux was varied by a factor of 3 or greater. Also, the macroscopic sample surface quality for the lower doping concentrations was found to be comparable to more heavily doped samples, as determined from inspection by optical microscope and laser reflection. Finally, all three studied families are chemically pristine when undoped and must be alloyed towards higher doping levels. Therefore, the opening of this gap towards lower concentrations cannot be associated with a degradation in crystal quality, as would be the case for the bismuth based cuprates. We note that ARPES studies of irradiated $Bi_2Sr_2CaCu_2O_{8+\delta}$ have also shown a demonstrable effect of induced disorder on the low energy spectral lineshape.

The compositional and doping dependence of $\Delta_{\text{LEG}}$ for all samples studied is summarized in Figure 3 and is shown to be reproducible over numerous measurements. In all compounds, $\Delta_{\text{LEG}}$ is largest at the lowest concentrations and closes with increasing doping. Despite the universal presence of this phenomenon, there exist obvious differences in the detailed behavior of each particular compound. In particular, the gap appears to close rapidly in $La_{2-x}Sr_xCuO_4$. Another intriguing point is that for $Ca_{1.9}Na_{0.1}CuO_2Cl_2$, which has a $T_c$ onset of 13 K, there still exists a small but finite $\Delta_{\text{LEG}} \sim 3$ meV above 15 K, the base temperature of our experiments. Interfamily variations in the behavior of $\Delta_{\text{LEG}}$ may not be unexpected, as many other physical properties exhibit considerable material-specific differences, including superconductivity and antiferromagnetism, and may depend on factors such as the chemical composition and crystal structure.

![FIG. 2: LEG spectra from hole-doped $Ca_{2-x}Na_xCuO_2Cl_2$ and $La_{2-x}Sr_xCuO_4$, and electron-doped $Nd_{2-x}Ce_xCuO_4$. The bottom inset shows the wavevector of the spectra taken from $Ca_{2-x}Na_xCuO_2Cl_2$ and $La_{2-x}Sr_xCuO_4$; the top shows $Nd_{2-x}Ce_xCuO_4$. All data were taken at 15 K.](image)
We now speculate on possible origins of the observed normal state gap. One very important consideration is that disorder is inherently manifest in the cuprates, as chemical substitution or intercalation is necessary for introducing carriers. At sufficiently low concentrations, the poor screening of these impurities could cause a strong disorder potential which may result in localization. The combination of disorder with long-range Coulomb interactions can produce a depression in the density of single-particle excitations at the chemical potential known as a Coulomb or “soft” gap, where the presence of repulsive electron-electron interactions necessitates a vanishing density of states at $E_F$ to ensure against an instability towards an excitonic ground state. The existence of disorder and localization may also be consistent with the reasonably broad peaks and edges, suggesting short lifetimes and/or breaking of translational symmetry resulting in poorly defined momentum eigenstates. Within this scenario, the reduction of $\Delta_{\text{LEG}}$ with doping can be explained by the enhancement of screening. It should be emphasized that the presence of a Coulomb gap even in the presence of disorder is still a non-trivial result, since gapless insulating behavior can also occur (i.e. weak localization); a Coulomb gap in the lightly doped cuprates would be a clear indication of the strong electron-electron interactions in these systems. It is also possible that a Coulomb gap may exist in the lightly doped cuprates without the aid of chemical disorder.

Recent STM studies have found considerable electronic inhomogeneity in the cuprate superconductors. In particular, results from Kohsaka et al. on Ca$_{1.93}$Nd$_{0.08}$CuO$_2$Cl$_2$ have shown that this inhomogeneity persists to high energy scales, implying that the distribution of carriers varies strongly on nanometer length scales. A recent neutron scattering study of lightly doped La$_2-x$Sr$_x$CuO$_4$ also suggests the presence of electronic phase separation below $x = 0.02$, close to where $\Delta_{\text{LEG}}$ vanishes. It is then possible that Coulomb blockade effects in mesoscopic systems such as granular metals may be germane to this discussion. Photoemission results from ultrathin granular Pb films and segmented one-dimensional systems have been interpreted within such a framework. We note that the observed values of $\Delta_{\text{LEG}}$ appear rather small for Coulomb blockade in the nanometer-sized patches proposed for the cuprates, although additional effects such as the mutual screening of patches and photohole relaxation may be mitigating factors. Whether this inhomogeneity is driven solely by the presence of chemical disorder or is an inherent property of the pristine CuO$_2$ plane is still unclear. Nevertheless, both chemical disorder and/or the presence of intrinsic electronic inhomogeneity are plausible origins for a Coulomb gap which may account for our results. We also note that the presence of $\Delta_{\text{LEG}}$ naturally reconciles the existence of an insulating ground state, as determined from collective transport properties, with the development of finite spectral weight near $E_F$ as measured from single-particle spectroscopy. It is now clear that although the spectral intensity of excitations near $E_F$ grows as a function of doping, these low-energy states are additionally gapped, resulting in a charge and thermal insulator.

Another intriguing possibility is that this may represent a signature of an alternate phase of matter. It has been proposed that the exotic normal state properties of the heavily underdoped cuprates may signify the presence of a competing order, such as a staggered flux phase or charge/spin stripes. It has also been established from neutron scattering that spin density wave (SDW) order exists in La$_{1.6-x}$Nd$_x$Sr$_2$CuO$_4$ and La$_2-x$Sr$_x$CuO$_4$. The fact that we have consistently observed this effect in multiple families suggests that if $\Delta_{\text{LEG}}$ is due to a competing order, this order should be generic to the cuprate superconductors. In a competing order scenario, the doping dependence in Figure 3 suggests that the strength of the competing phase decreases rapidly as a function of doping, similar to the behavior of the pseudogap. We note that the presence of chemical or electronic disorder does not necessarily preclude the existence of a competing order. Future experiments may help to clarify this situation. For instance, a systematic study of $\Delta_{\text{LEG}}$ with increasing chemical impurities, such as Zn or Ni substitution, or induced disorder, would elucidate the effects of disorder on this gap, and help to distinguish between a soft gap or a competing order scenario.

In summary, we have presented ARPES results revealing the existence of a finite gap over the entire Brillouin zone of the lightly doped cuprates in the low-temperature normal state. This phenomenon was observed in both electron and hole-doped cuprates and was found to decrease as a function of carrier doping. We believe this effect is one of the keys underlying the novel superconductor-insulator transition in the lightly doped region of the phase diagram and may represent electronic inhomogeneity/disorder effects or a competing order parameter in the lightly doped regime. It is hoped that these results will spur future activity into developing a better understanding of the properties of the lightly doped cuprates.

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