NMR Evidence for a d-Wave Normal-State Pseudogap

G. V. M. Williams,[1] J. L. Tallon,[1] E. M. Haines,[1] R. Michalak,[2] and R. Dupree[2]
[1]*New Zealand Institute for Industrial Research, P.O. Box 31310, Lower Hutt, New Zealand*
[2]*Department of Physics, University of Warwick, Coventry CV4 7AL, United Kingdom*
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NMR data from high-T_c superconducting cuprates having widely different $T_{c,\max}$ values and different hole concentrations, p, are shown to implicate a d-wave-like pseudogap. The deduced pseudogap energies agree well with the gap in the charge excitations determined from photoemission measurements, and the gap energies scale with $T_{c,\max}$. The pseudogap and superconducting gap thus have the same energy scale and for different cuprates have a universal p dependence. [S0031-9007(96)02205-3]

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Recent angle-resolved photoemission spectroscopy (ARPES) measurements [1] on underdoped $Bi_2Sr_2CaCu_2O_{8+\delta}$ indicated the presence of a gap in the charge excitation spectrum existing above T_c. This confirms the normal-state pseudogap inferred from Knight shift [2], heat capacity [3], infrared [4], and transport [5,6] data on $YBa_2Cu_3O_{7-\delta}$. Although its origin is not understood, the pseudogap is intimately linked with superconductivity: It is generic to the cuprates, its magnitude decreases with increasing hole concentration [3,5,7] while, at the same time, T_c rises, and the pseudogap scales with $T_{c,\max}$ (Ref. [8]). Any theory for the superconducting cuprates will need to account for the pseudogap. In the nearly antiferromagnetic Fermi-liquid phenomenological theory it is assumed that a gap exists only in the imaginary part of the dynamic susceptibility at the antiferromagnetic wave vector, $\mathbf{q} = (\pi, \pi)$ [9]. This is inconsistent with the ARPES experimental data, where a gap is found in the charge excitations [1]. Loram *et al.* [7] have recently shown that the heat capacity and magnetic susceptibility above T_c can be analyzed in terms of a normal-state pseudogap having d-wave symmetry. They also showed, using Wilson's ratio $(S_{\mathrm{el}}/\chi_s T)$, that spin and charge excitations make comparable contributions to the entropy, and hence there is no separate spin gap. The recent ARPES measurements now confirm this picture: Like the superconducting gap [10–12], the normal-state gap probably has $d_{x^2-y^2}$ symmetry [1].

In this paper we analyze NMR data from $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$ (Ref. [8]), $La_{2-x}Sr_xCaCu_2O_6$ (Ref. [8]), $Y_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$, $HgBa_2CuO_{4+\delta}$, $Tl_2Ba_2CaCu_2O_{8-\delta}$ (Ref. [13]), $YBa_2Cu_4O_8$ (Ref. [14]), $YBa_2Cu_3O_{7-\delta}$ (Refs. [15,16]), and $HgBa_2Ca_2Cu_3O_{8-\delta}$ (Ref. [17]) in both the d-wave and s-wave normal-state gap scenarios. We show that a d-wave-like pseudogap can describe both the superconducting and normal-state Knight shifts, consistent with the above-noted heat capacity, susceptibility, and ARPES measurements. The preparation and experimental details of the ^{89}Y NMR measurements on $Y_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ and the ^{17}O NMR measurements on $HgBa_2CuO_{4+\delta}$ are presented elsewhere [8,18].

The appearance of a normal-state gap can be seen in the NMR shifts plotted in Figs. 1, 2, and 3 for $HgBa_2CuO_{4+\delta}$, $Tl_2Ba_2CaCu_2O_{8-\delta}$ (Ref. [13]), and $YBa_2Cu_4O_8$ (Ref. [14]). At optimal hole concentration these have maximum T_c values of 96 K, 110 K, and 93 K, respectively. The decreasing NMR shift with decreasing temperature is unexpected for a metal and is attributed to the existence of a pseudogap in the normal state. For example, the Fermi contact interaction from s-state hyperfine coupling in metals leads to a Knight shift that is proportional to the static spin susceptibility [19], χ_s, and because the Pauli spin susceptibility is proportional to the density of states at the Fermi level, $N(E_F)$, the Knight shift should be proportional to $N(E_F)$. For a metal with a constant density of states near the Fermi level the resultant NMR shift is temperature independent.

We modeled the NMR data in Figs. 1, 2, and 3 by noting that previous NMR measurements have

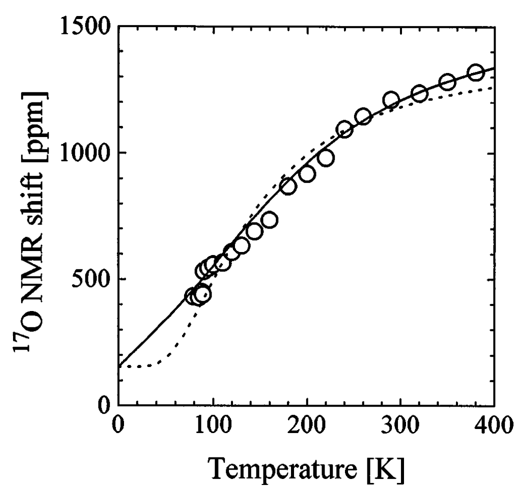

FIG. 1. The temperature dependence of the ^{17}O NMR shift for $HgBa_2CuO_{4+\delta}$. The solid line is a fit to the data assuming d-wave superconducting and normal-state gaps, while the dotted line is a fit to the data assuming a d-wave superconducting gap and an s-wave normal state gap.

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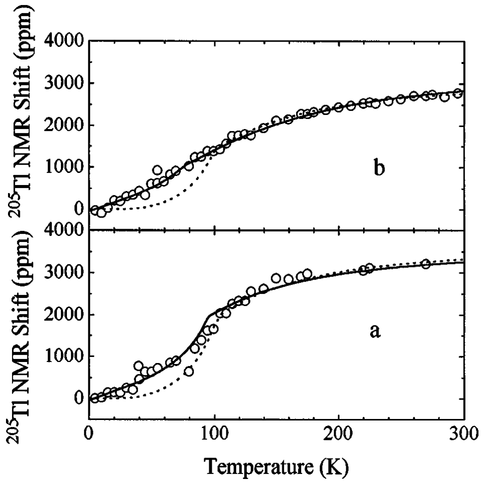

FIG. 2. The temperature dependence of ^{205}Tl(2) NMR shift for $Tl_2Ba_2CaCu_2O_{8-\delta}$ with (a) $T_c = 99$ K and (b) $T_c = 85$ K (Ref. [13]). The ^{205}Tl(2) resonance originates from ^{205}Tl which has partially substituted from the site between the CuO_2 planes. In both cases $\Delta_T(0)/k_B T_{c,\max}$ is taken as 4. The solid line and dotted lines are as in Fig. 1.

shown that the ^{63}Cu, ^{17}O, ^{89}Y (Ref. [20]), and ^{205}Tl (Ref. [13]) NMR shifts are all proportional to the static susceptibility. From the Mila-Rice Hamiltonian [21] it can be shown that the NMR shifts can be expressed as $K_s = \sum_j A_j \chi_s / g\mu_B + \sigma$ where A_j are the hyperfine coupling constants, χ_s is the static spin susceptibility, g is the electron g factor, μ_B the Bohr magneton, and σ is the temperature-independent chemical shift. The Pauli spin susceptibility is obtained from perturbation theory [22] and can be expressed as $\chi_s = \mu_B \int_{-\infty}^{\infty} N(E)[-\partial f(E)/\partial E]dE$, where $N(E)$ is the density of states and $f(E)$ is the Fermi function. The effect of antiferromagnetic correlations experimentally observed in neutron scattering experiments [23] is accounted for in a mean-field approach leading to a static spin susceptibility, $\chi_s^* = \chi_s/(1 - \lambda\chi_s)$, where λ is related to the spin-spin exchange energy. We have previously fitted temperature-dependent Knight shift data assuming a simple step-function density of states [2]. Here, the density of states is derived from $N(E) = \int \delta(E - E(\mathbf{k}))d\mathbf{k}^2/2\pi^2$ in a manner similar to Loram *et al.* [24] by writing the quasiparticle energies as $E(\mathbf{k}) = [\varepsilon(\mathbf{k})^2 + \Delta_T(\mathbf{k})^2]^{1/2}$, where $\Delta_T(\mathbf{k})^2 = \Delta(\mathbf{k})^2 + E_g(\mathbf{k})^2$ with $\Delta(\mathbf{k})$ being the superconducting gap and $E_g(\mathbf{k})$ being the normal-state gap. The experimental values [25] for $2\Delta/k_B T_{c,\max}$ at zero Kelvin range from 6 to 9 and are greater than expected from the weak-coupling BCS theory where $2\Delta/k_B T_{c,\max} = 3.53$ for s-wave symmetry [22] and 4.28 for d-wave symmetry [26] of the superconducting gap. Consequently, strong-coupling calculations are more appropriate for the cuprates. However, as the functional form of $\Delta(T)$ is similar for strong and weak coupling theories [27], we use the BCS temperature dependence of $\Delta(T)$ to model the NMR data. We start with the BCS gap equation [22] $\Delta(\mathbf{k}) = -\sum_{\mathbf{k}'} V(\mathbf{k},\mathbf{k}')\Delta(\mathbf{k})[1 - 2f(|E(\mathbf{k}')|)]/2E(|\mathbf{k}'|)$ and use $E_g(\mathbf{k}) = E_g$ for an s-wave pseudogap and $E_g(\mathbf{k}) = E_g(\cos(2\theta))$ for a d-wave pseudogap. Recent experiments have shown that the superconducting gap has d-wave symmetry [10–12], thus we model it as $\Delta(\mathbf{k}) = \Delta(\cos(2\theta))$. The resultant $\Delta_T/\Delta_T(0)$ is plotted in the inset of Fig. 3 for both the s-wave and d-wave models for various values of $E_g/\Delta_T(0)$. It can be seen that there is no significant difference in the curves. ^{63}Cu NMR Knight shift measurements [28] on $YBa_2Cu_3O_{7-\delta}$, where E_g is less than T_c, have shown that the data below T_c can be fitted to a d-wave superconducting gap with $2\Delta(0)/k_B T_{c,\max} = 8$. Moreover, electronic heat capacity [24], infrared reflectivity [29], and Raman [30] and ARPES [1] studies all show that $\Delta_T(0)$ remains independent of hole concentration *across the underdoped region.* Consequently, we use $\Delta_T(0) = 4k_B T_{c,\max}$ to fit all of the NMR data. The density of states is obtained by assuming a 2D cylindrical hole Fermi surface, where $\varepsilon(\mathbf{k})$ is taken as $\varepsilon(\mathbf{k}) = (h/2\pi)^2 k^2/2m^*$.

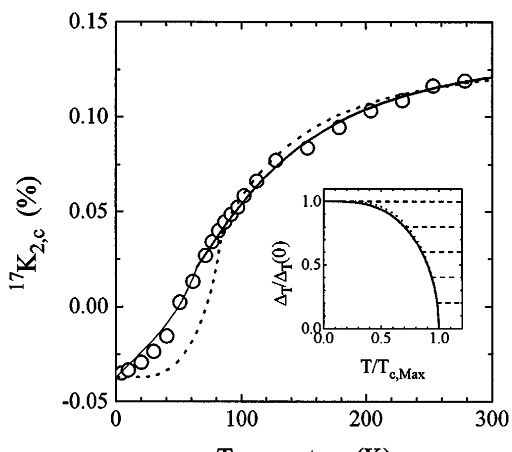

FIG. 3. The temperature dependence of the ^{17}O NMR shift from the O_2 oxygen in the CuO_2 plane with H parallel to the c axis for $YBa_2Cu_4O_8$ with $T_c = 81$ K (Ref. [14]). The solid line and dotted lines are as in Fig. 1. Inset: the temperature dependence of the total gap Δ_T scaled by the total gap at $T = 0$, $\Delta_T(0)$. The solid curve is the d-wave BCS solution, and the dotted curve is the s-wave solution. The dashed lines indicate the normal-state gap.

The effect of pseudogap symmetry on $N(E)$ can be seen in Fig. 4, where in (a) we plot $N(E)$ for a d-wave pseudogap and in (b) $N(E)$ is plotted for an s-wave pseudogap. A d-wave superconducting gap and d-wave pseudogap result in a linear $N(E)$ about the chemical potential both above and below T_c, while a d-wave superconducting gap and a s-wave pseudogap lead to $N(E)$ being zero up to E_g both above and below T_c. It can be seen in Figs. 1, 2, and 3 that a d-wave normal-state pseudogap gives a better fit (solid curves) to the data than the s-wave fits (dashed curves) both above T_c (Fig. 1) and especially below T_c (Figs. 2 and 3). The linear NMR shift at low temperatures is consistent with the linear $N(E)$ expected

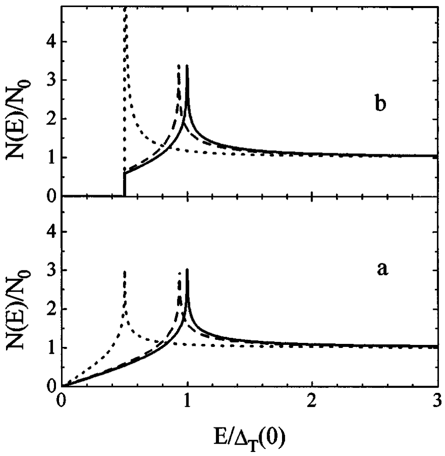

FIG. 4. Plot of the $N(E)$ against energy for (a) a d-wave normal-state gap and a d-wave superconducting gap, and (b) a s-wave normal-state gap and a d-wave superconducting gap. The density of states is scaled by $N_0 = m^*/\pi(h/2\pi)^2$, and the energy is scaled by the total gap at $T = 0$, $\Delta_T(0)$. The values of $T/T_{c,\max}$ are 0 (solid line), 0.5 (dashed line), and 1 (dotted line).

for a d-wave superconducting gap in combination with a d-wave normal-state gap.

Fitting the data above T_c to an s-wave pseudogap gives E_g values of up to 330 K, and hence it would be expected that such a superconductor should be semiconducting above T_c with the resistivity decreasing exponentially with increasing temperature due to thermal excitation of carriers across the gap. However, this is not what is observed [31,32]. For optimally doped cuprates, where E_g is comparable to T_c, the resistivity increases linearly with temperature. By contrast, in the underdoped compounds the resistivity is linear near room temperature and remains so until below a certain temperature [$\sim$180 K for $YBa_2Cu_4O_8$ (Ref. [32])] where there appears a deviation to lower resistivities originally attributed to the opening of a "spin gap" [32].

In Fig. 5 we plot the normal-state pseudogap energy obtained by fitting the $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$ (Ref. [8]), $La_{2-x}Sr_xCaCu_2O_6$ (Ref. [8]), $Y_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$, $HgBa_2CuO_{4+\delta}$, $Tl_2Ba_2CaCu_2O_{8-\delta}$ (Ref. [13]), $YBa_2Cu_4O_8$ (Ref. [14]), $YBa_2Cu_3O_{7-\delta}$ (Refs. [15,16]), and $HgBa_2Ca_2Cu_3O_{8-\delta}$ (Ref. [17]) Knight shift data to the d-wave normal-state pseudogap model. The pseudogap energies are scaled by $T_{c,\max}$. For all except $La_{2-x}Sr_xCaCu_2O_6$, the hole concentration, p, was estimated from the relation $T_c/T_{c,\max} = 1 - 82.6(p - 0.16)^2$ that has been found to approximate many of the high-T_c superconducting cuprates [33]. For $La_{2-x}Sr_xCaCu_2O_6$, p was taken as $x/2$, which is in fact close to the value estimated from this relation [8]. It can be seen that $E_g \sim k_BT_{c,\max}$ close to optimal doping ($p \sim 0.16$) while E_g exceeds $\Delta(0)$ for $p < 0.11$.

We also show in Fig. 5 the pseudogap energies obtained from ARPES measurements on $Bi_2Sr_2CaCu_2O_{8+\delta}$ (filled circles [1]), where, again, the hole concentra-

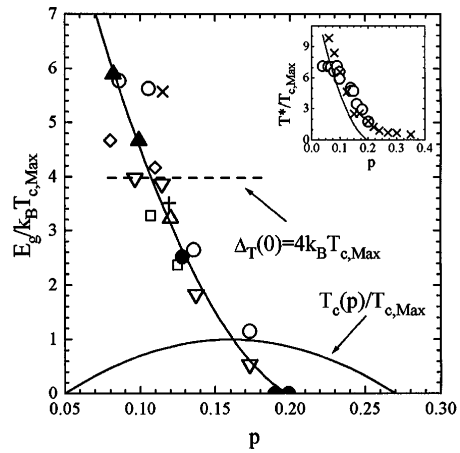

FIG. 5. The hole concentration dependence of the normal-state pseudogap energy, E_g, scaled by $k_BT_{c,\max}$. E_g values were obtained by fitting the NMR data from (○) $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$ (Ref. [8]), (◇) $La_{2-x}Sr_xCaCu_2O_6$ (Ref. [8]), (▲) $Y_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$, (×) $HgBa_2CuO_{4+\delta}$, (□) $Tl_2Ba_2CaCu_2O_{8-\delta}$ (Ref. [13]), (△) $YBa_2Cu_4O_8$ (Ref. [14]), (▽) $YBa_2Cu_3O_{7-\delta}$ (Refs. [15,16]), and (+) $HgBa_2Ca_2Cu_3O_{8-\delta}$ (Ref. [17]) to the d-wave model described in the text. Also included is E_g from ARPES measurements on $Bi_2Sr_2CaCu_2O_{8+\delta}$ (●). The solid curve is a polynomial fit to the data. Inset: values of $T^*/T_{c,\max}$ determined from (○) susceptibility [5], and (×) thermoelectric power [36] measurements on $La_{2-x}Sr_xCuO_4$. The solid curve reproduces the polynomial fit to $E_g/k_BT_{c,\max}$.

tions were estimated from the relation $T_c/T_{c,\max} = 1 - 82.6(p - 0.16)$ [2]. The $E_g/k_BT_{c,\max}$ values obtained from ARPES measurements are consistent with those determined from NMR measurements, indicating that the gap measured from NMR data is a gap in the charge excitations and not due to a distinct gap in the spin excitations.

Batlogg and coauthors [5] have examined the temperature dependence of the magnetic susceptibility, Hall coefficient, and resistivity as a function of doping and determine a crossover temperature, T^*, which they associate with the opening of the pseudogap. In order to compare their T^* with our E_g values we note that, if the criterion they used to determine T^* from the susceptibility is applied to the d-wave model for χ_s, we find $E_g/k_B \sim 0.4T^*$. We have taken their data and show in the inset in Fig. 5 that $0.4T^*/T_{c,\max}$ (circles) is comparable to our fitted $E_g/k_BT_{c,\max}$ values. Cooper and Loram [34] have carried out a similar scaling analysis on the thermoelectric power, $S(T)$, for $La_{2-x}Sr_xCuO_4$ and have determined T^* values for different values of $p = x$. These T^* values are plotted in the inset in Fig. 5 as $T^*/T_{c,\max}$. On the underdoped side there is a close correspondence between their T^* values (shown as crosses) and our E_g values which underscores the association of T^* with the energy scale of the normal-state pseudogap. The fact that T^* is nonzero in the overdoped region and becomes independent of hole concentration does not necessarily mean that the pseudogap persists over the entire overdoped region. Indeed, our NMR data suggest that it does not. If

$E_g = 0$, $S(T)$ still must exhibit a peak, and therefore an apparent finite T^*, because S is thermodynamically required to be zero at $T = 0$.

Several important conclusions may be drawn for the above results. (i) The present analysis suggests that T^* is not a temperature at which the normal-state pseudogap opens but is the energy scale for the gap. (ii) The similar p dependence of $E_g/k_B T_{c,\max}$ for the single CuO_2 layer $La_{2-x}Sr_xCuO_4$ superconductors and the double CuO_2 layer superconductors indicates that the normal-state pseudogap is common to all of the cuprates and not just related to coupling between the CuO_2 layers in the double CuO_2 layer cuprates. (iii) The fact that E_g scales with $T_{c,\max}$ suggests that its energy scale is set neither by J, the antiferromagnetic superexchange energy, nor by the Fermi energy, E_F, but by the same energy scale as governs the pairing interaction.

There are striking similarities between the pseudogap as described herein and the superconducting gap: they have the same symmetry, energy scale, and phonon frequencies renormalize [30] with the opening of either gap. However, there is no phase transition associated with the pseudogap, and the depressed spectral weight in the normal state is not transferred to a zero-frequency delta function but is shifted to higher frequencies [4]. Emery and Kivelson [35] have proposed that the pseudogap state corresponds to short-range pairing correlations which appear below a mean-field transition temperature T_c^{MF}. Phase fluctuations in the underdoped regime prevent long-range phase coherence until some lower temperature T_θ which is therefore the upper limit for the actual T_c. In their picture, T_c^{MF} decreases with increasing hole concentration while T_θ increases and eventually they cross, yielding the well-known approximately parabolic p dependence of T_c. In this scenario, the pseudogap and superconducting gaps naturally have the same symmetry and energy scale. However, the present data suggest that E_g and $\Delta_T(0)$ are not so intimately related. These two gap energies have a very different Zn and Ni substitutional dependence [2], very different p dependence, and Fig. 5 shows that E_g falls essentially to zero at about $p \sim 0.2$ while superconductivity persists to rather higher hole concentrations ($p \sim 0.27$ for $La_{2-x}Sr_xCuO_4$). It is also difficult to see how T_c^{MF} can increase with underdoping when experimental evidence shows that $\Delta_T(0)$ remains constant.

In conclusion, our analysis of a broad range of NMR data for underdoped cuprates implies that the normal-state pseudogap has d-wave-like symmetry in the sense that the density of states is similar to that for a d-wave gap. These results are consistent with recent ARPES data and show that the depression in the static spin susceptibility is due to a gap in the total spectrum and not a gap in just the spin spectrum. By considering samples with widely differing $T_{c,\max}$ values (ranging from 39 to 135 K) we find E_g scales with $T_{c,\max}$, and therefore the pseudogap and superconducting gaps have the same energy scale. We note the strong similarity of the phase behavior shown in Fig. 5 to that of a charge density wave competing with superconductivity [36].

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